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VINYLTRIMETHYLENE

AND

TRIMETHYLENEMETHANE

BY



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A THESIS

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The undersigned certify that they have read and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled VINYLTRIMETHYLENE AND TRIMETHYLENEMETHANE submitted by Douglas M. Cameron, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

The thermal isomerization of vinylcyclopropane to cyclopentene has been suggested to involve a vinyltrimethylene intermediate. Evidence has been provided that 1-pyrazoline gives an intermediate, upon thermolysis, that is similar to the intermediate involved in the cyclopropane to propylene isomerization. In this investigation the thermolysis of 3-vinyl-1-pyrazoline, which is prepared by the addition of diazomethane to butadiene, is used as an alternate route to vinyltrimethylene.

The thermolysis products are vinylcyclopropane (98.9%) and cyclopentene (0.9%) with trace amounts of the pentadienes. The yields show that closure of the intermediate to vinylcyclopropane is much more rapid than closure to cyclopentene, which is consistent with the observations of cis- trans- isomerizations in various 1,2-disubstituted cyclopropanes by other investigators. 3-Vinyl-1-pyrazoline has an activation energy for thermolysis that is 10.2 kcal. lower than that for 1-pyrazoline due to allylic resonance stabilization of the rate-determining transition state. The observation of a secondary kinetic isotope effect in the thermolysis of 3-vinyl-1-pyrazoline-5,5-d₂ indicates that both carbon-nitrogen bonds cleave in the rate-determining step even though one of them is allylic. A nmr spectrum of the cyclopentene-d₂ produced showed that all of the deuterium is in the 4-position, which

indicates that cyclopentene arises directly from the intermediate, rather than from a "hot" vinylcyclopropane. However, a "hot" vinylcyclopropane results when 3-vinyl-1-pyrazoline-5,5- d_2 is thermolyzed above 160° as evidenced by higher yields of cyclopentene and the pentadienes, the formation of new products (butadiene and cyclopentadiene), and scrambling of deuterium in the cyclopentene- d_2 that is produced.

Previous studies on thermolysis of 1-pyrazolines suggested that 4-methylene-1-pyrazoline would produce trimethylenemethane, a species of considerable theoretical interest. Preparation of this pyrazoline was accomplished by addition of diazomethane to allene in ether solution. Thermolysis ($E_a = 32.6 \pm 0.3 \text{ kcal.mole}^{-1}$, $\Delta S_{250}^\ddagger = -1.1 \pm 0.6 \text{ e u.}$) gives only methylenecyclopropane and nitrogen. When 4-methylene-1-pyrazoline-3,3- d_2 is thermolyzed, the products are methylenecyclopropane-2,2- d_2 (59.3%) and methylenecyclopropane-4,4- d_2 (40.7%) rather than 66.7% of the former and 33.3% of the latter as expected if trimethylenemethane is an intermediate. However, the results of thermolysis of 4-methylene-1-pyrazoline-3,3,6,6- d_4 reveal that the unexpectedly high yield of the latter product is due to an isotope effect in the product-determining step. Studies on secondary kinetic isotope effects indicate that simultaneous cleavage of both carbon-nitrogen bonds occurs in the rate-determining step. All of the aforementioned

observations support the intermediacy of trimethylenemethane; however, whether it exists in the singlet state or undergoes intersystem crossing to its triplet ground state is not known.

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CHAPTER I

H I S T O R I C A L

(A) Thermolysis of Pyrazolines

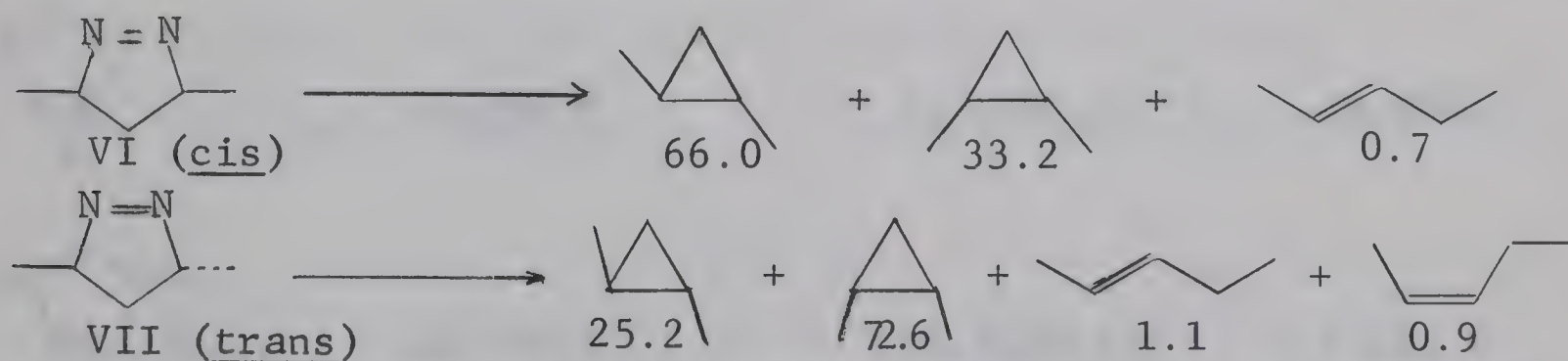
Many investigators have suggested a trimethylene diradical species as an intermediate in the isomerization of cyclopropane to propylene. Recently the investigation of 1-pyrazoline as an alternative source of the same intermediate has been undertaken.¹⁻⁵ Various methylated 1-pyrazolines were thermolyzed, in the temperature range 185-280°, to produce cyclopropanes and olefins. The kinetic parameters are shown in Table I.

Methyl substitution in the 3 or 5 position of pyrazolines produces a decrease of 1.2 ± 0.2 kcal. per methyl group in the activation energy. Since the activation energies for thermolysis of VI and VII were about equal to that of V, it was suggested that both carbon-nitrogen bonds were breaking simultaneously in the rate-determining step. If the bonds broke separately, then II and VI as well as V, VIII, and IX should have similar activation energies, but this was not observed.

That elimination of nitrogen was the slow step of the thermolysis was shown by control experiments whereby attempts to interconvert VI and VII failed. More conclusive evidence that the rate-determining step was the elimination of nitrogen to yield a hydrocarbon intermediate was obtained by comparison

of the rates and products of thermolysis of 4-methyl-1-pyrazoline (III) and 4-methyl-1-pyrazoline-4-d (XII).^{1,2,5} No large kinetic isotope effect in the rate determining step (k_1) was observed; however, there was a large isotope effect in the product-determining step (k_2). Therefore the cyclopropane and olefin products had to arise from a common intermediate. The intermediate must arise after the rate determining step and by virtue of the kinetic data in Table II, be free of nitrogen.

More information about the intermediate was obtained from the yields of the various products of thermolysis of VI and VII. The trans-pyrazoline (VII) gives rise to mainly cis-1,2-dimethylcyclopropane whereas cis-pyrazoline (VI) forms mainly trans-1,2-dimethylcyclopropane. The nature of the products in-



dicates that the two terminal carbon atoms of the intermediate are not completely free of each other's influence. The formation of cyclopropanes and olefins was explained as arising from an intermediate having the terminal methyl

TABLE I

KINETIC PARAMETERS OF 1-PYRAZOLINE AND METHYL SUBSTITUTED

1-PYRAZOLINE THERMOLYSIS

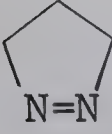
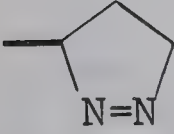
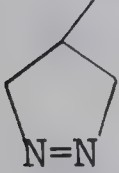

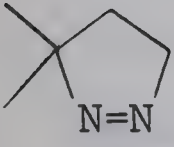
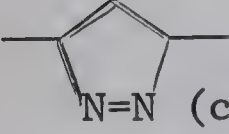
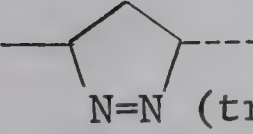
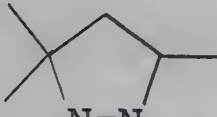
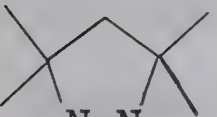
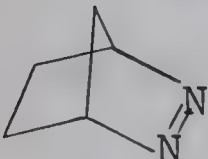
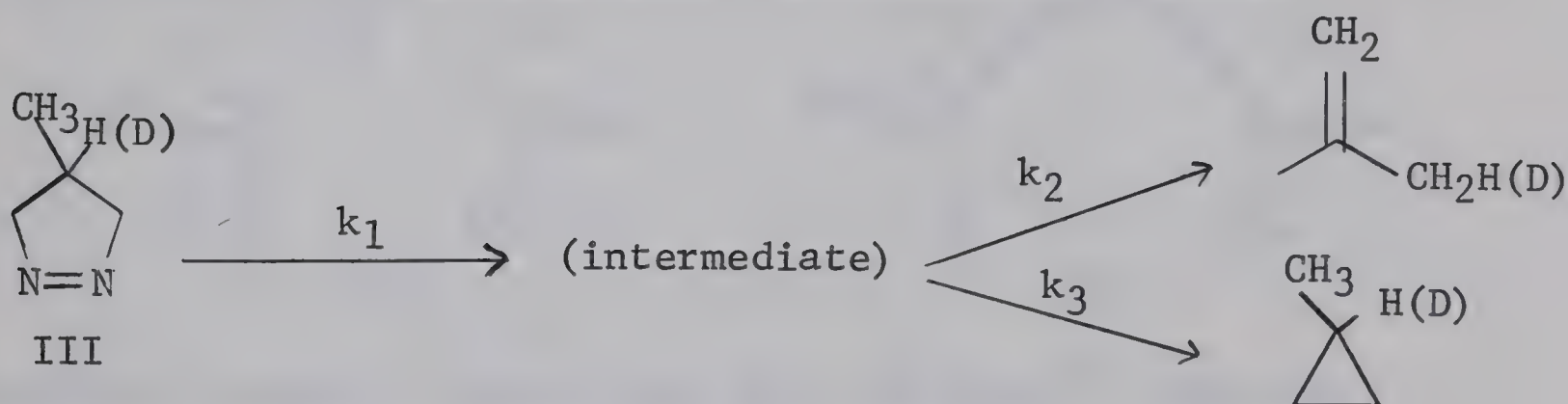
Compd.	Ea (kcal.)	Log A	ΔS^\ddagger_{250} (e.u.)
 I	42.4 \pm 0.3	15.93 \pm 0.13	11.2 \pm 0.6
 II	41.0 \pm 0.3	15.7 \pm 0.15	10.1 \pm 0.7
 III	42.2 \pm 0.2	15.85 \pm 0.05	10.8 \pm 0.3
 IV	42.8 \pm 0.2	14.10 \pm 0.07	2.9 \pm 0.3
 V	40.0 \pm 0.2	15.85 \pm 0.3	10.8 \pm 0.2
 VI (cis)	40.3 \pm 0.3	15.54 \pm 0.11	9.4 \pm 0.5
 VII (trans)	40.2 \pm 0.3	15.67 \pm 0.11	10.0 \pm 0.5

TABLE I (Continued)

Compd.	Ea (kcal.)	Log A	$\Delta S^\ddagger_{250}(\text{e.u.})$
 VIII	39.0 ± 0.4	15.42 ± 0.21	8.9 ± 0.9
 IX	37.7 ± 0.4	14.49 ± 0.12	4.6 ± 0.8
 X	36.9 ± 0.2	14.74 ± 0.10	5.8 ± 0.5



$k_{2H}/k_{3H} = 47.7/52.3$ and $k_{2D}/k_{3D} = 34.0/66.0$;
 then $k_{2H}/k_{3H}k_{2D} = 1.80 \pm 0.08$, $k_{1H}/k_{1D} = 1.07 \pm 0.03$

TABLE II

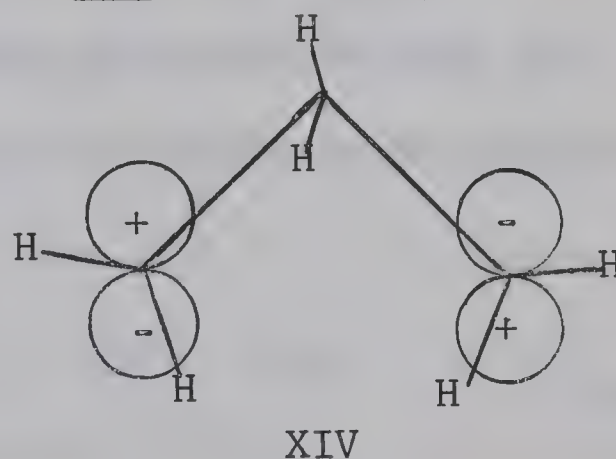
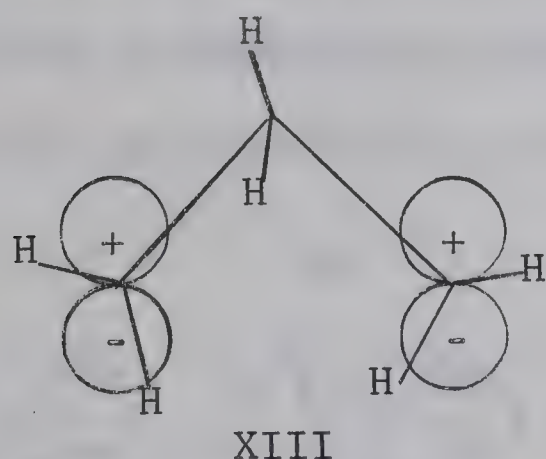
EFFECT OF DEUTERIUM SUBSTITUTION IN III AT 241.75°C

Compd.	$10^4 k (\text{sec}^{-1})$	% cyclopropane	% 2-methylpropene
III	64.1 ± 0.6	52.3 ± 0.3	47.7 ± 0.3
XII	59.5 ± 0.6	66.0 ± 0.3	34.0 ± 0.4

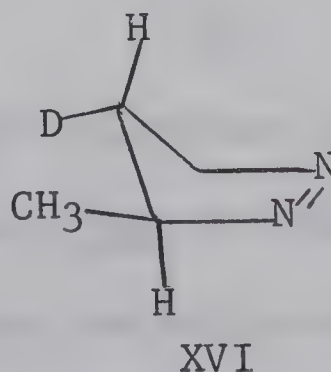
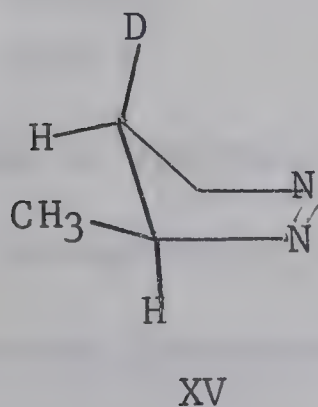
groups on C₃ and C₅ in the plane defined by C₃, C₄, and C₅. Such an intermediate can exist as a singlet state species having the

symmetry of XIII and XIV. A conrotatory⁶ mode of ring closure of XIV would explain the major products produced from the thermolysis of VI and VII. Hoffmann has carried out extended Huckel molecular orbital calculations on these systems and has suggested that XIV is more stable than XIII. The species XIII is also that predicted by application of Woodward - Hoffmann rules for electrocyclic transformations.

More information about the symmetry of the intermediate was obtained from the thermolysis of cis- and trans-4-

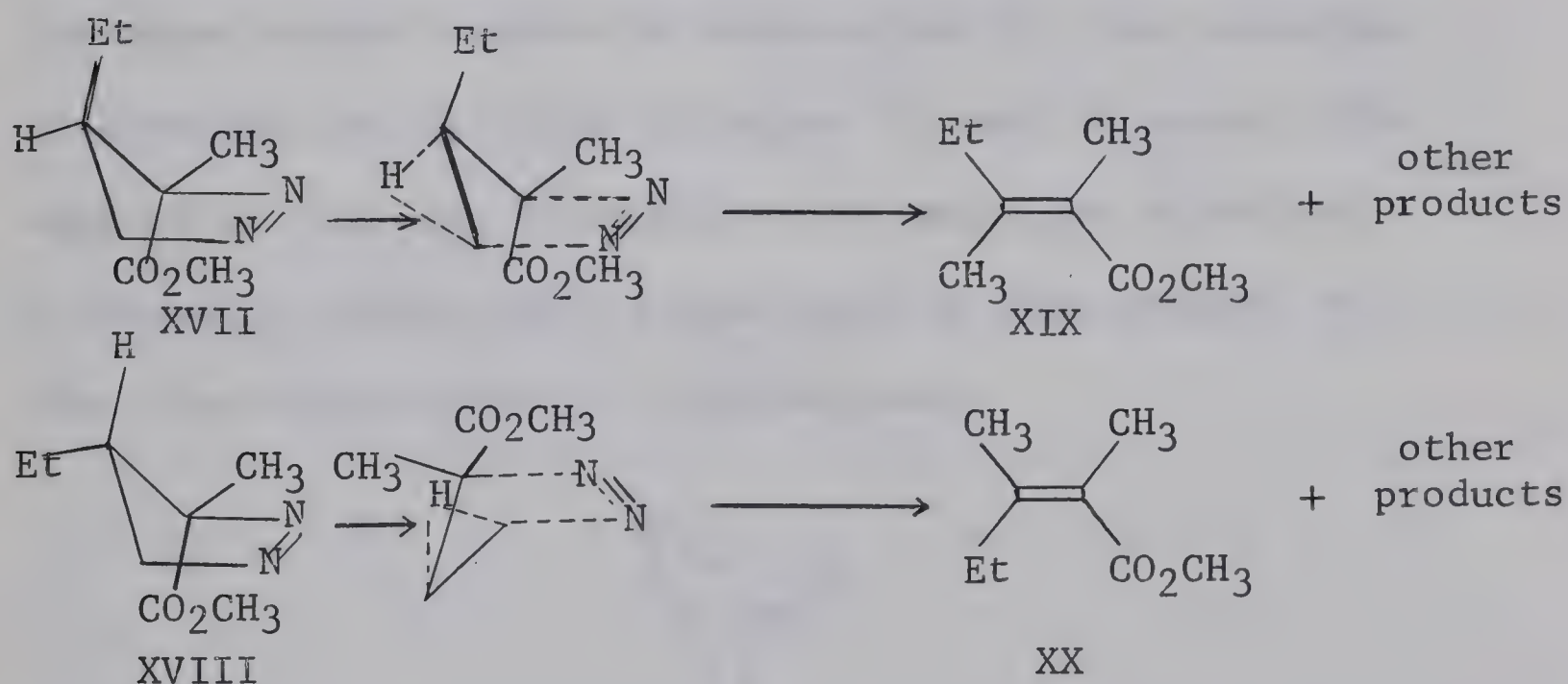


deuterio-3-methyl-1-pyrazoline (XV) and (XVI)⁸. Earlier, McGreer and Wu⁹ obtained good evidence for hydrogen migration concerted with nitrogen elimination in the olefin formation



ing reaction when XVII and XVIII were thermolyzed. Their

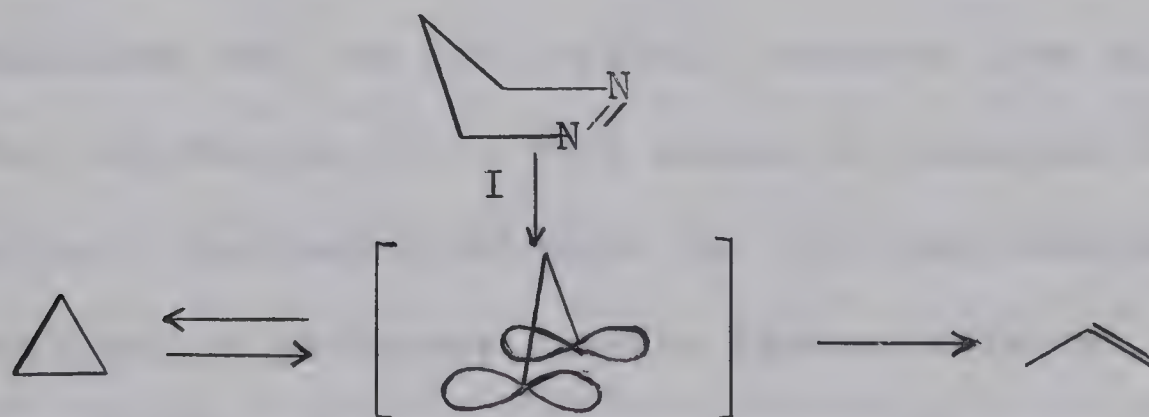
conclusions were based on the observation that only one substituted 2-pentenoic acid derivative (XIX and XX) was formed in each case rather than a mixture of the two. Although McGreer and Wu's experiments were done in solution on compounds which contained an electron withdrawing group, their mechanism had to be considered in terms of the thermolysis of alkyl-1-pyrazolines in the gas phase. By thermolysis of XV and XVI, Erickson⁸ was able to distinguish between McGreer and Wu's mechanism and the mechanism involving a symmetrical intermediate proposed earlier by Mishra.¹ An examination of the gaseous products by nuclear



magnetic resonance (nmr) for the deuterium label was made. The integration ratios for cis- and trans-2-butene and 1-butene indicated that hydrogen and deuterium migrate with equal propensity from both of the isomeric pyrazolines (XV

and XVI) as predicted by Mishra's mechanism.

Evidence that the intermediate produced by the thermolysis of 1-pyrazolines also plays a role in the isomerization of cyclopropanes to olefins was obtained by comparing the yield of propylene (10.8%) relative to cyclopropane on the thermolysis of I with that predicted by Benson.³⁴ From calculations based on the intermediacy of the trimethylene diradical in the isomerization of cyclopropane and from methylene addition to ethylene, Benson predicted that such an intermediate would partition into about 90% cyclopropane and 10% propylene in agreement with the experimental results of Rabinovitch.³⁵ The preceding observation and the data in Tables III and IV support the suggestion that the intermediate trimethylene diradical produced by cyclopropane thermolysis is very similar to that from thermolysis of 1-pyrazolines.



(B) Secondary Kinetic Isotope Effects

The question of whether cleavage of both carbon-nitrogen

TABLE III

COMPARISON OF BUTENE PROPORTIONS FROM THERMOLYSIS OF
3-METHYL-1-PYRAZOLINE (II) AND METHYLCYCLOPROPANE

Reagent	Temp. (°C.)	1-butene	<u>cis-2-</u> <u>butene^a</u>	<u>trans-2-</u> <u>butene^a</u>
II ⁸	250	1.0	0.63	0.34
Methylcyclopropane	400	1.0	0.71	0.30
Methylcyclopropane	469	1.0	0.63	0.28
(a) Relative to 1-butene				

TABLE IV

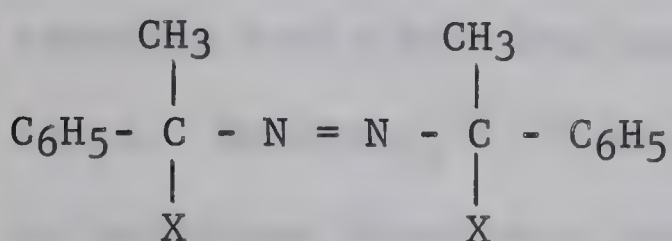
COMPARISON OF OLEFINIC PRODUCT PROPORTIONS FROM THERMOLYSIS
3,3-DIMETHYL-1-PYRAZOLINE (V) AND 1,1-DIMETHYLCYCLOPROPANE

Compd.	Temp. (°C.)	2-Methyl- 2-Butene	3-Methyl ^a - 1-Butene	2-Methyl ^a - 1-Butene
V	202	1.0	0.85	trace
1,1-dimethylcyclopropane	447	1.0	1.06	0.018
(a) Relative to 2-methyl-2-butene				

bonds occurs simultaneously or separately during thermolysis of alkylpyrazolines was not conclusively answered from kinetic data. Part of Chapter II of this thesis is directed at obtaining more conclusive evidence for the simultaneous cleavage by observations on secondary kinetic isotope effects.

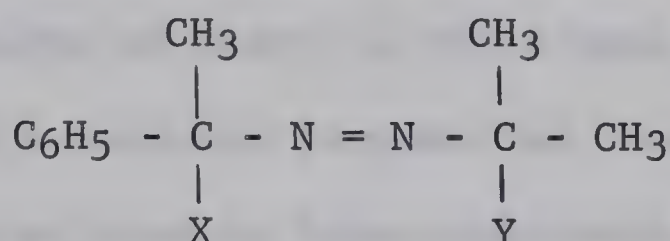
Seltzer¹¹⁻¹⁴ has used secondary kinetic isotope effects to estimate the degree of bond-breaking that occurs in the

transition state during the thermolysis of various symmetrical and unsymmetrical azocompounds. He found, on comparing azobis- α -phenylethane (XXIa) with azobis- α -phenylethane- α,α' -d₂ (XXIb), an isotope effect, $k_{XXIa}/k_{XXIb} = 1.27$, which suggested that both carbon-nitrogen bonds were breaking in a simultaneous process. Decomposition of α -phenylethylazo-2-propane (XXII) presented a somewhat different picture. The



XXIa, X = H

XXIb, X = D

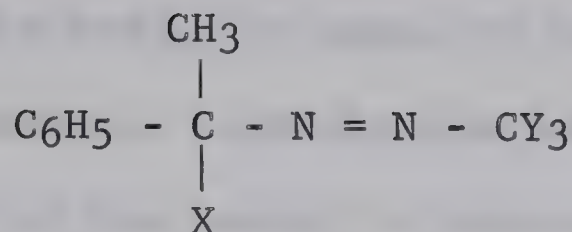


XXIIa, X = Y = H

XXIIb, X = D, Y = H

XXIIc, X = H, Y = D

secondary effects, $k_{XXIIa}/k_{XXIIb} = 1.16$ and $k_{XXIIa}/k_{XXIIc} = 1.04$, led to the conclusion that here too, both carbon-nitrogen bonds stretch in the transition state but to unequal degrees. In a third and less symmetrical case, α -phenylethylazomethane (XXIIIa), α -phenylethyl- α -d-azomethane (XXIIIb) and α -phenylethylazomethane-d₃ (XXIIIc) were thermolyzed. A comparison of rates, $k_{XXIIIa}/k_{XXIIIb} = 1.13$ and $k_{XXIIIa}/k_{XXIIIC} = 0.97$, led to the conclusion that the slow step involved rupture of only the α -phenylethyl carbon-nitrogen bond. Rupture of the methyl-carbon bond had to occur in a subsequent fast step.



XXIIIIa, X = Y = H

XXIIIIb, X = D, Y = H

XXIIIIc, X = H, Y = D

It is possible to calculate kinetic isotope effects from a knowledge of the geometry and force constants in the reactant state and from assumptions of those in the transition state. Wolfsberg^{15,16} has made a computer program for "exact" calculations based on a program written by Schachtschnieder¹⁷ which calculated normal harmonic vibrational frequencies from given force constants, masses and positions of atoms. It should be noted that "exact" refers to the precision in the calculations rather than to its relation to "exact" reality. The "exact" calculations arise as a result of a complete assessment of all the parameters involved in the Bigeleisen equation.^{18,19}

$$\frac{k_H}{k_D} = \frac{K_H}{K_D} \left(\frac{\nu_{H,L}^\ddagger}{\nu_{D,L}^\ddagger} \right) \times \frac{S_H/S_D}{S_H^\ddagger/S_D^\ddagger} \times \frac{\prod_i \frac{u_{D,i}}{u_{H,i}} e^{(u_{H,i} - u_{D,i})/2}}{\prod_i \frac{u_{D,i}^\ddagger}{u_{H,i}^\ddagger} e^{(u_{H,i}^\ddagger - u_{D,i}^\ddagger)/2}} \frac{(1 - e^{-u_{H,i}})}{(1 - e^{-u_{D,i}})} \frac{(1 - e^{-u_{H,i}^\ddagger})}{(1 - e^{-u_{D,i}^\ddagger})}$$

Here K is the transmission coefficient, S the symmetry number, $\nu_{H,L}/\nu_{D,L}$ the ratio of frequencies along the

reaction co-ordinate and μ_i is equal to $h\nu_i/kt$.

Seltzer has used the Bigeleisen equation to enable him to get an estimate of the amount of hybridization change that occurs in the transition state during the potassium thiocyanate catalyzed isomerization of maleic acid.²⁰ The inverse secondary α -deuterium isotope effect was measured over a temperature range of 15 to 80°. From the slope of a plot of the log of the measured isotope effect versus $1/T$, the net change in the carbon-hydrogen vibrational frequencies in going from the ground state to the transition state was evaluated. On comparing this data with the total net change of 565 cm^{-1} accompanying the change from sp^3 to sp^2 hybridization, as determined by Streitwieser et al,²¹ he estimated that the transition state lies a little more than halfway along the path between a trigonal and tetrahedral carbon atom.

A similar conclusion was reached when calculations were made for the isotope effect for thermolysis of XXI.¹⁴ The calculated and observed α -effects fitted best when all bending force constants associated with nitrogen were reduced in the transition state to 40% of their original value.

(C) Isomerization of Vinylcyclopropane

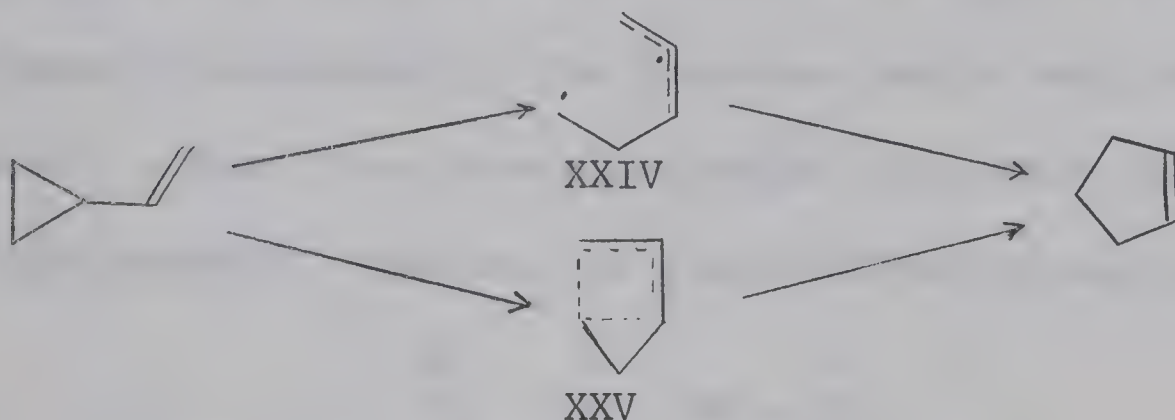
The thermal isomerizations of cyclopropane and alkylcyclopropanes to olefins are among the best known examples of unimolecular reactions. They have been described in terms of a transition state involving a diradical²², or in terms of a complex where hydrogen migration occurs simultaneously with carbon-carbon bond rupture.²³

Geometrical isomerizations of 1,2-dialkylcyclopropanes have been found to occur and are most frequently explained by a diradical mechanism.²⁴

Another type of cyclopropane isomerization was observed when vinylcyclopropanes were heated above 300°²⁵⁻²⁸. Wellington²⁶ found that the isomerization of vinylcyclopropane was a unimolecular, first-order and essentially homogeneous process which was unaffected by addition of nitric oxide. It yielded mainly cyclopentene together with small amounts of 1,4-pentadiene and cis- and trans-1,3-pentadiene. The activation energies (kcal./mole) were found to be: over-all process, 50.0 ± 0.3 ; formation of cyclopentene, 49.7 ± 0.3 ; 1,4-pentadiene, 57.3 ± 1.0 ; cis-1,3-pentadiene, 56.2 ± 0.8 ; trans-1,3-pentadiene, 53.6 ± 0.8 . They were all significantly lower than that for the cyclopropane isomerization to propylene (65.0 kcal.).³⁰ It was suggested that the transition state was stabilized by a contribution from the

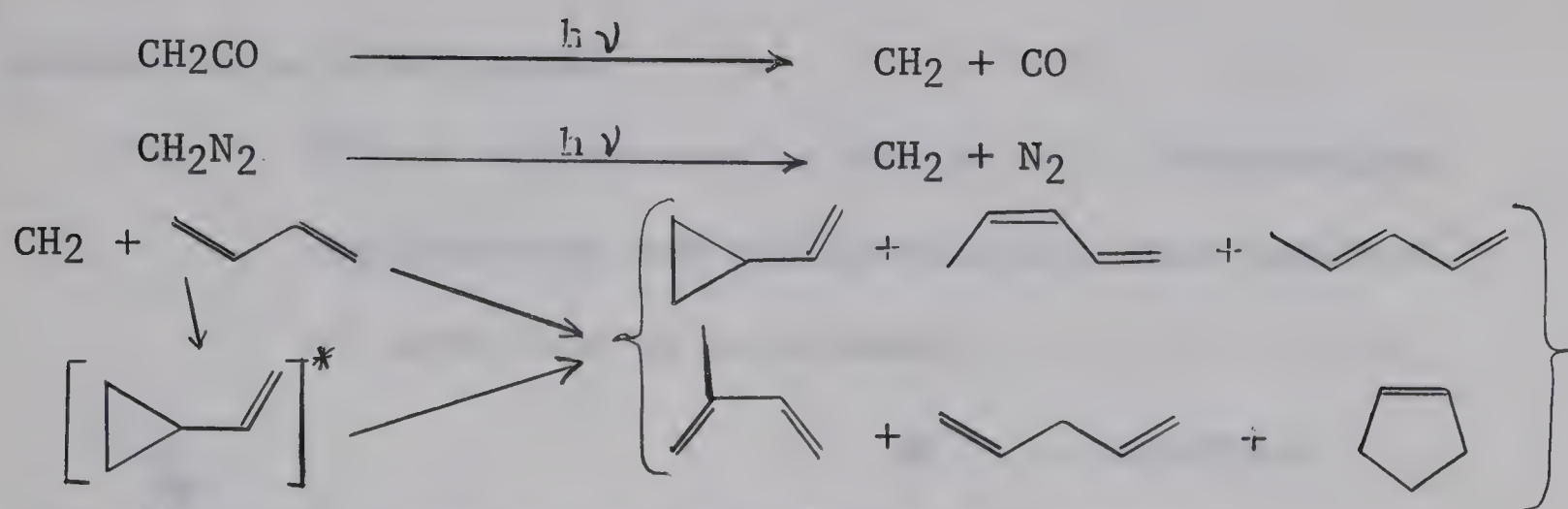
allylic resonance energy resulting in the lower activation energies.

It is not known as yet whether the vinylcyclopropane thermolysis proceeds via a two-step mechanism involving a diradical (XXIV) or by a concerted process involving a five membered ring (XXV). Part of the goal of the present work is to obtain more information about the mechanism by arriving at a similar diradical intermediate through the thermolysis of

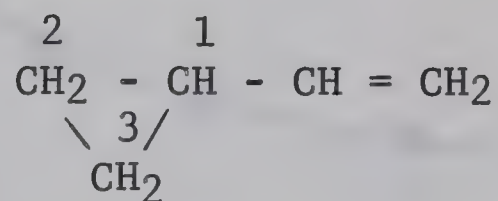


3-vinyl-1-pyrazoline.

An intermediate similar to XXIV is also possible in the study by Frey³¹ of the reactions of a "hot" vinylcyclopropane, produced by the addition of methylene to butadiene. This species underwent various unimolecular isomerizations to give cyclopentene, 1,4-pentadiene, cis-1,3-pentadiene and trans-1,3-pentadiene. Some of the cyclopentene was sufficiently vibrationally excited to undergo decomposition to cyclopentadiene and hydrogen. At the higher pressures (>200 torr) the major portion of the excess energy of the intermediate was removed by collisional deactivation to yield vinylcyclopropane. However, at lower pressures



isomerization competed favorably with collisional deactivation. Some insertion of methylene into the carbon-hydrogen bonds was also observed, but was found to be pressure independent. The isoprene which was observed apparently arose from insertion rather than from the "hot" vinylcyclopropane, because its yield did not change with

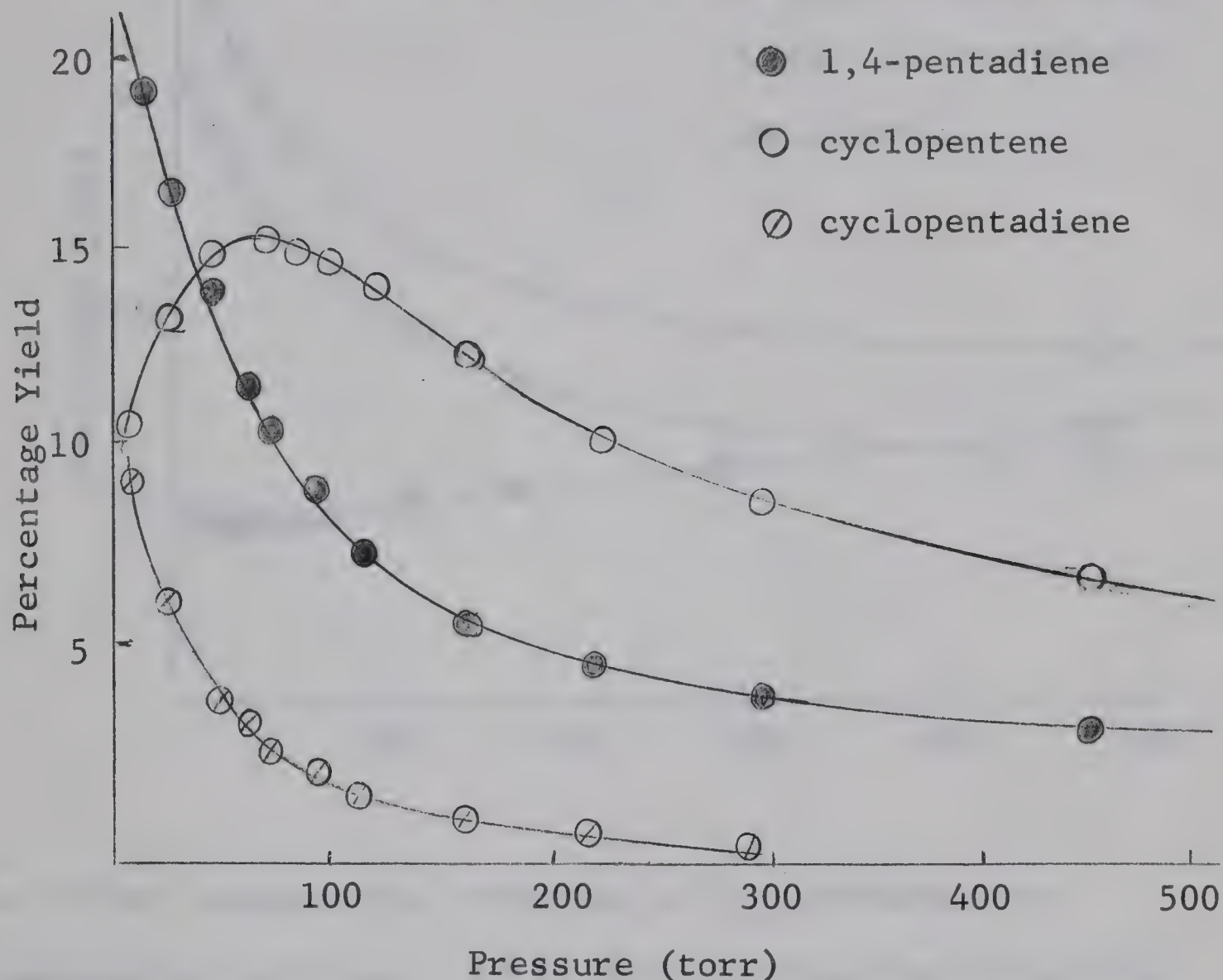


pressure. Therefore, isomerizations from the "hot" vinylcyclopropane occurred via cleavage of the C₁-C₂ or C₁-C₃ bonds only. The "virtual diradicals" formed by cleavage of these bonds could be stabilized by allylic resonance, while the species formed from cleavage of the C₂-C₃ bond, which would eventually give isoprene, could not.

Examples of the pressure dependence of the products are shown in Fig. 1 and Fig. 2. The percentage yield of vinylcyclopropane at a given pressure may be obtained by subtracting the total yield of the products shown at that

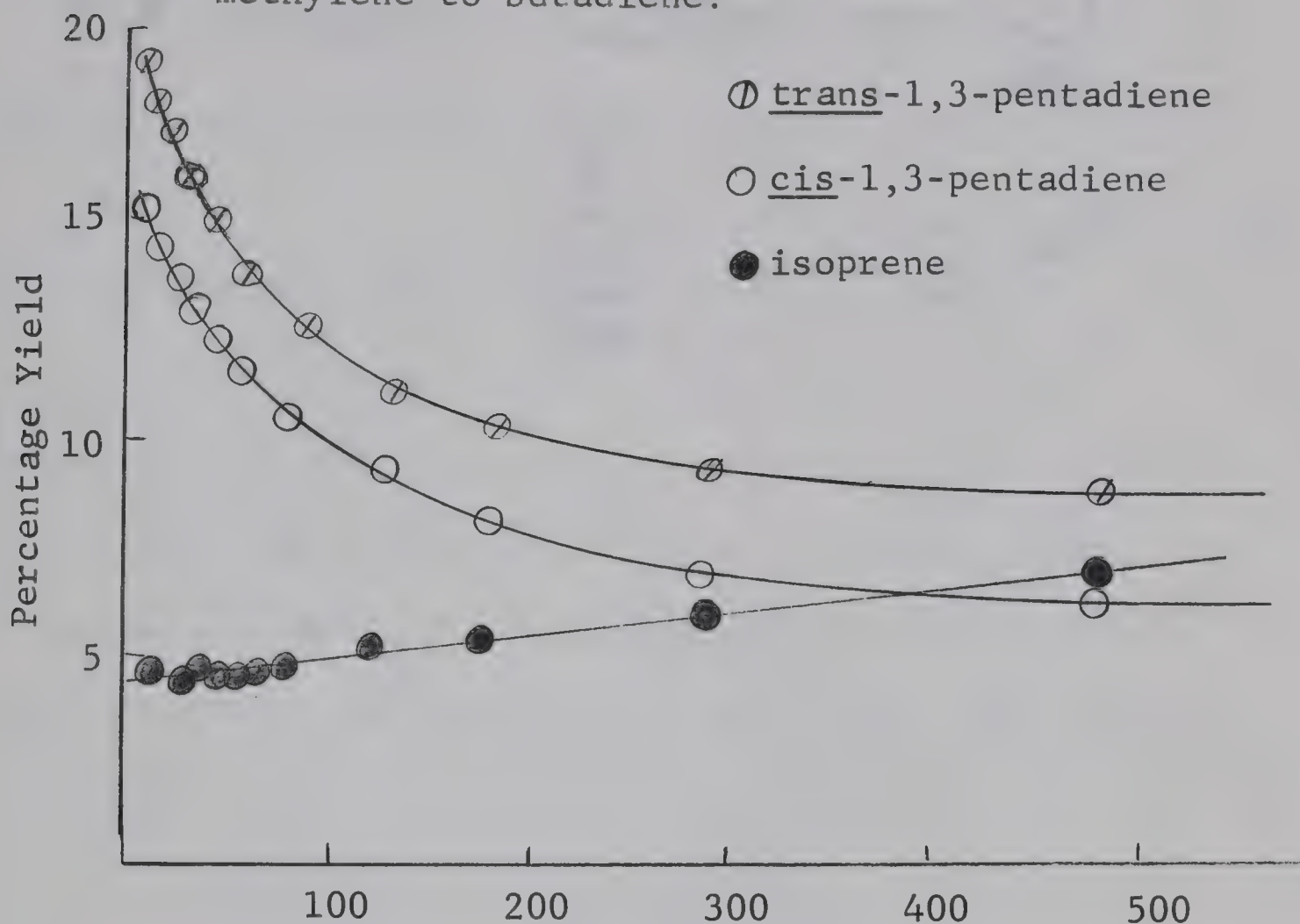
pressure from one-hundred

Fig. 1 Effect of pressure on yields of 1,4-pentadiene, cyclopentene and cyclopentadiene from addition of methylene to butadiene.



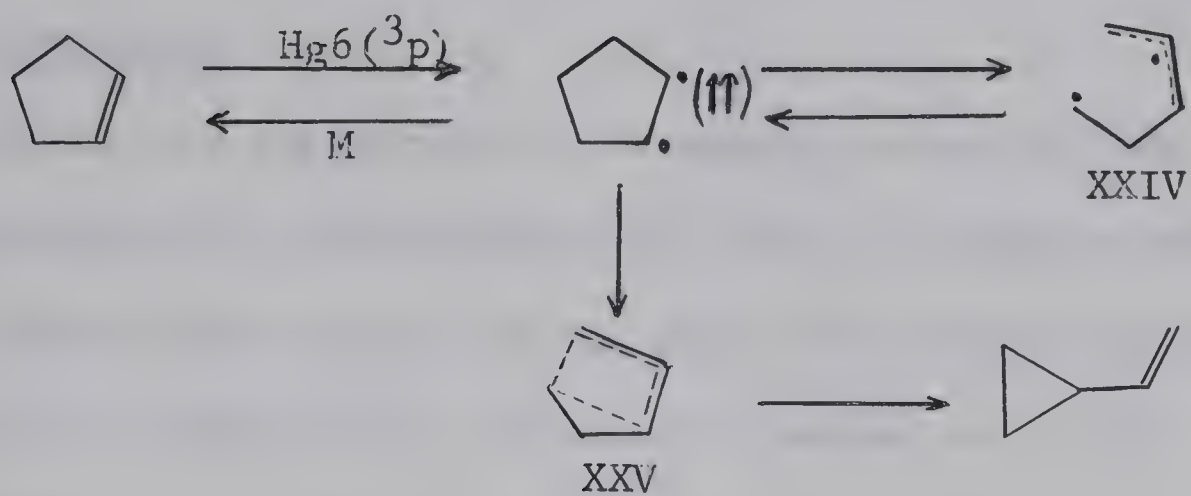
In a study of the mercury photosensitized decomposition of cyclopentene^{32,33} it was found that vinylcyclopropane was the major product. Again, there is a possibility that vinyltrimethylene (XXIV) or a similar species may be involved as an intermediate. However, if such a species was formed, it would have to have a very short lifetime because the yield of vinylcyclopropane was unaffected by the addition

Fig. 2 Effect of pressure on the yields of isoprene, cis and trans-1,3-pentadiene from addition of methylene to butadiene.



of 6% NO, whereas the formation of C₁₀ products was completely inhibited. It is believed that the first step in the isomerization was the formation of an excited triplet state of cyclopentene. The formation of vinylcyclopropane must have involved cleavage of the B-carbon-carbon bond of the cyclopentene ring. Whether this occurred via an intermediate vinyltrimethylene or by direct isomerization in which one bond was broken as the other was

being formed, could not be determined experimentally.

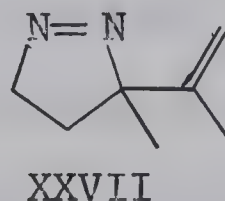
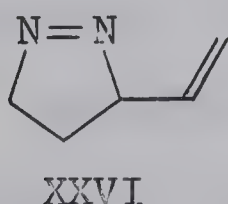


CHAPTER II

3-VINYL-1-PYRAZOLINE - SYSTHESIS AND THERMOLYSIS

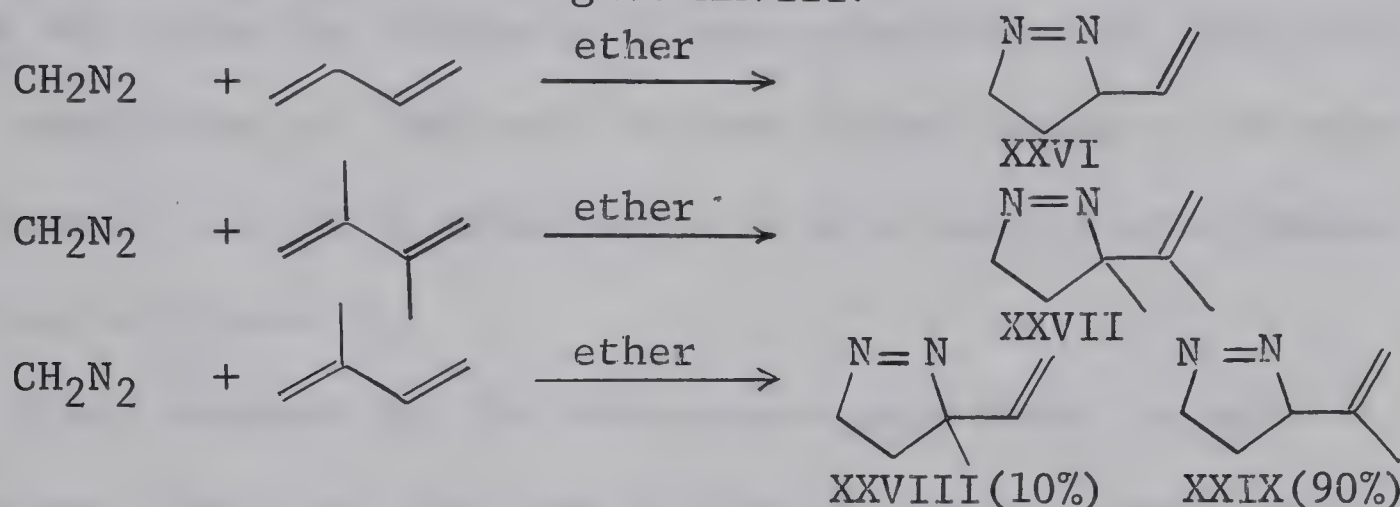
(A) Syntheses

There are three methods frequently used for the preparation of 1-pyrazolines; (a) the 1,3 dipolar addition of a diazoalkane to an olefin, (b) the reaction of hydrazine with a 1,3-dihaloalkane followed by oxidation of the resulting pyrazolidine, and (c) the reaction of an α,β -unsaturated aldehyde or ketone with hydrazine to give a 2-pyrazoline, which upon reduction to the pyrazolidine is subsequently oxidized to the 1-pyrazoline. 3-Vinyl-1-pyrazoline (XXVI) and 3-methyl-3-isopropenyl-1-pyrazoline (XXVII) were both prepared by the first method.



In 1932 Muller and Roser³⁷ added diazomethane to butadiene to produce a vinylpyrazoline. However, it is not evident whether the product was XXVI or its tautomer 5-vinyl-2-pyrazoline. In the present investigation a two-fold excess of butadiene in an ether solution of diazomethane was sufficient to affect the preparation of XXVI in an 80% yield in 12 hours. In order to prepare XXVII it was necessary to add 2,3-dimethyl-1,3-butadiene to a concentrated ether solution of diazomethane and to let the mixture stand

for at least three days before completion, as judged by the disappearance of the yellow color. When isoprene was used a similar reluctance to add to the more highly substituted double bond was observed. The addition of diazomethane to the unsubstituted double bond to form XXIX was found to be nine times that of the rate of addition to the methyl substituted double bond to give XXVIII.



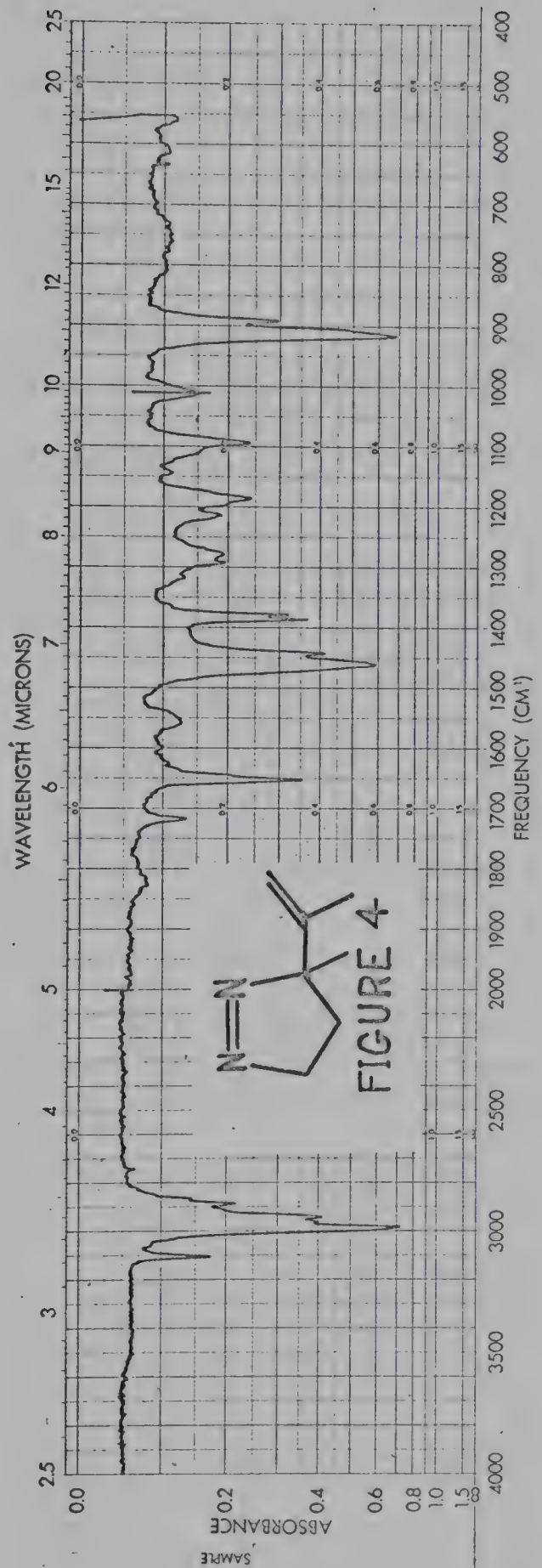
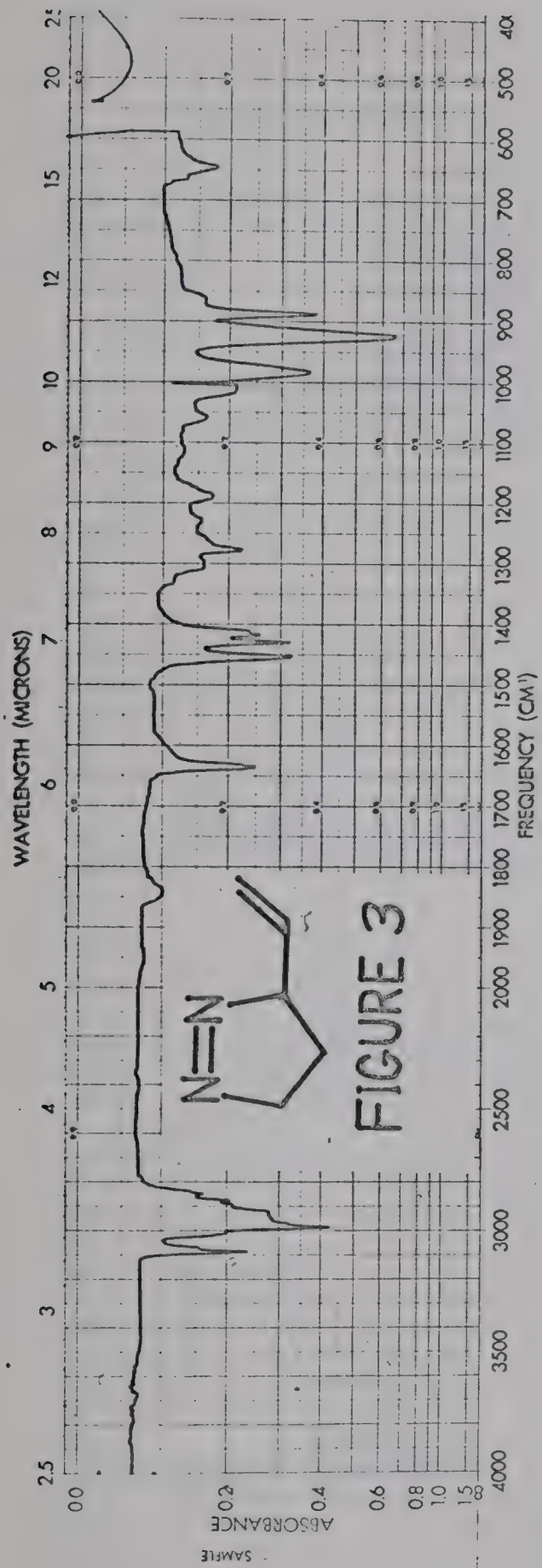
The pyrazolines have to be kept in the absence of air.

Exposure for only a few minutes is enough to produce a yellow coloration. Prolonged standing at room temperature causes tautomerization to the 2-pyrazoline. Therefore, XXVI and its methyl derivatives were stored in the cold under an atmosphere of nitrogen.

Proof of the structure of XXVI was obtained in the following manner. Microanalysis is consistent with a formula $\text{C}_5\text{H}_8\text{N}_2$. The compound decomposes on heating to give nitrogen and hydrocarbon products typical of 1-pyrazolines. The products obtained can all be explained as arising from a compound of structure XXVI. The ultraviolet spectrum had a λ_{max} at 322 mμ ($E=336$, $\text{C}_2\text{H}_5\text{OH}$) typical of 1-pyrazolines.

There is no absorption in the infrared spectrum (CCl_4 , Figure 3) above 3100 cm^{-1} , which indicates the absence of nitrogen-hydrogen bonds in the molecule. The peak at 3090 cm^{-1} , is typical of the vinylic carbon-hydrogen bond stretching vibration and the absorption at 1635 cm^{-1} is consistent with the carbon-carbon double bond stretching mode. The presence of an azo group is indicated by weak absorption at 1540 cm^{-1} . (The absorption at 1540 cm^{-1} is not strong enough to be seen in Figure 3 but it is observed in a more concentrated sample such as in Figure 9.)

Final support for the structure comes from its nmr spectrum. The A-60 spectrum (Figure 5) appears very complicated because of its large number of lines. However, when the 100 Mc spectrum was obtained at a sweep width of 100 c.p.s. (Figure 6) it was possible to measure all of the chemical shifts and coupling constants, as shown in Table 5. The integration ratios (Figure 5) were found to be 3:3:2 for the olefinic to allylic to saturated protons as expected for XXVI. McGreer et al³⁸ suggest that a dihedral angle of about 25° exists between the $\text{C}_3\text{C}_4\text{C}_5$ and $\text{C}_3\text{C}_5\text{NN}$ planes in the 1-pyrazoline ring on the basis of coupling constants between the protons at C_4 and those at C_3 and C_5 , as observed in the nmr spectra of the 1-pyrazolines that they studied. The coupling constants in XXVI are similar to those quoted by McGreer, thus it is likely



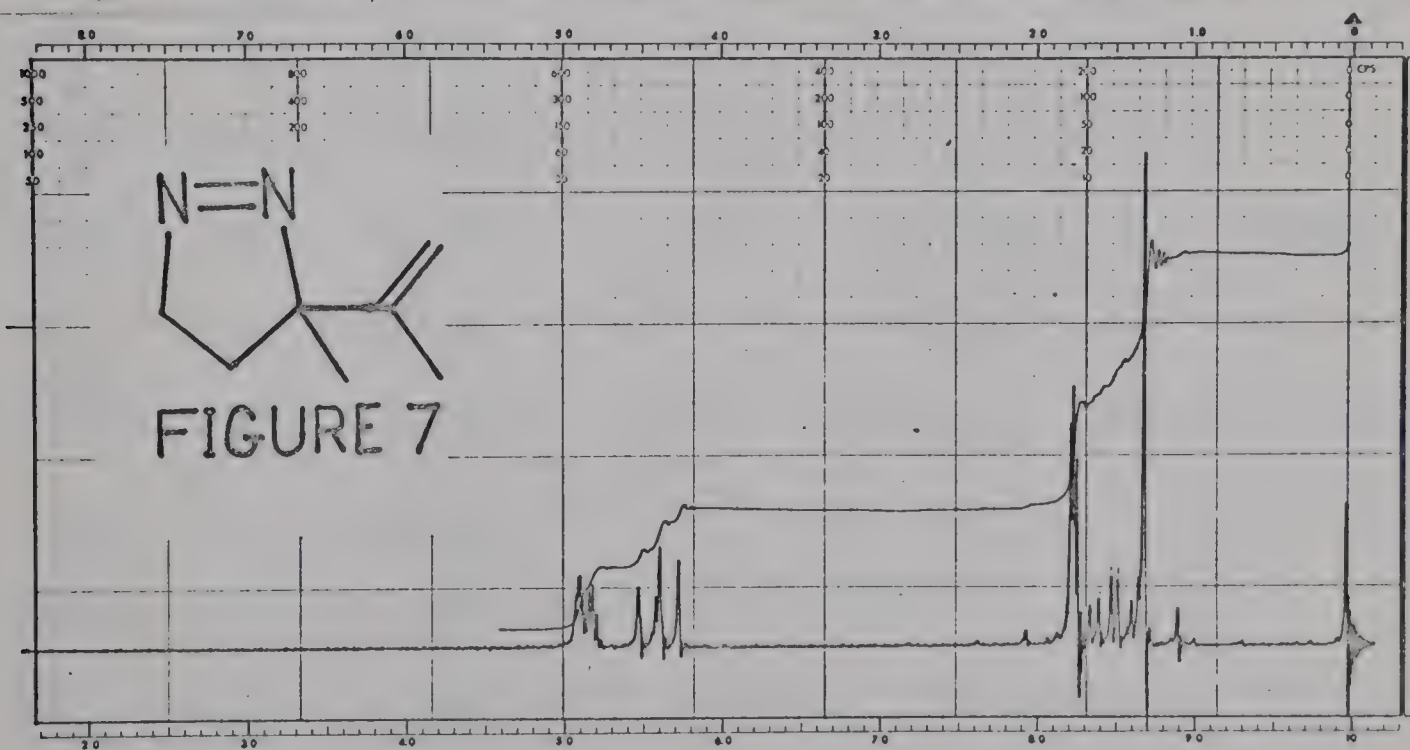
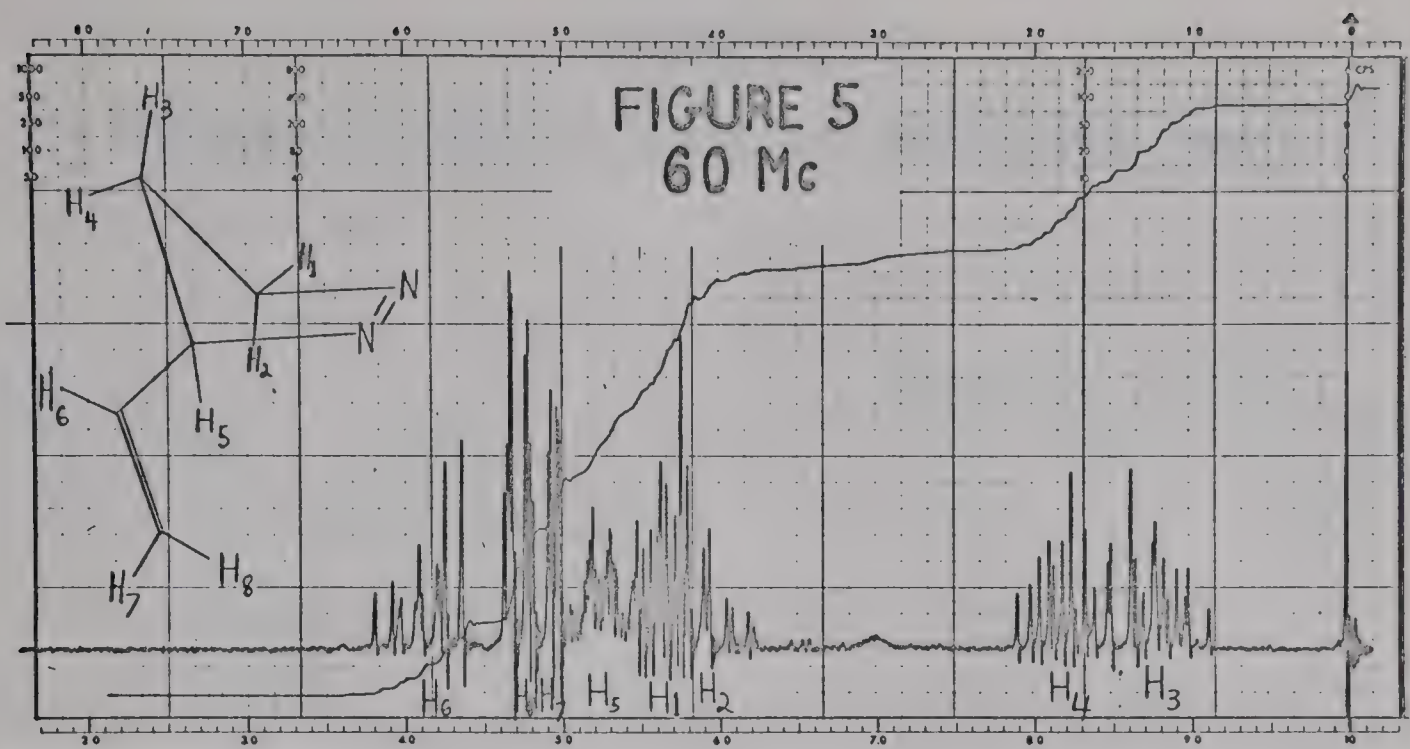
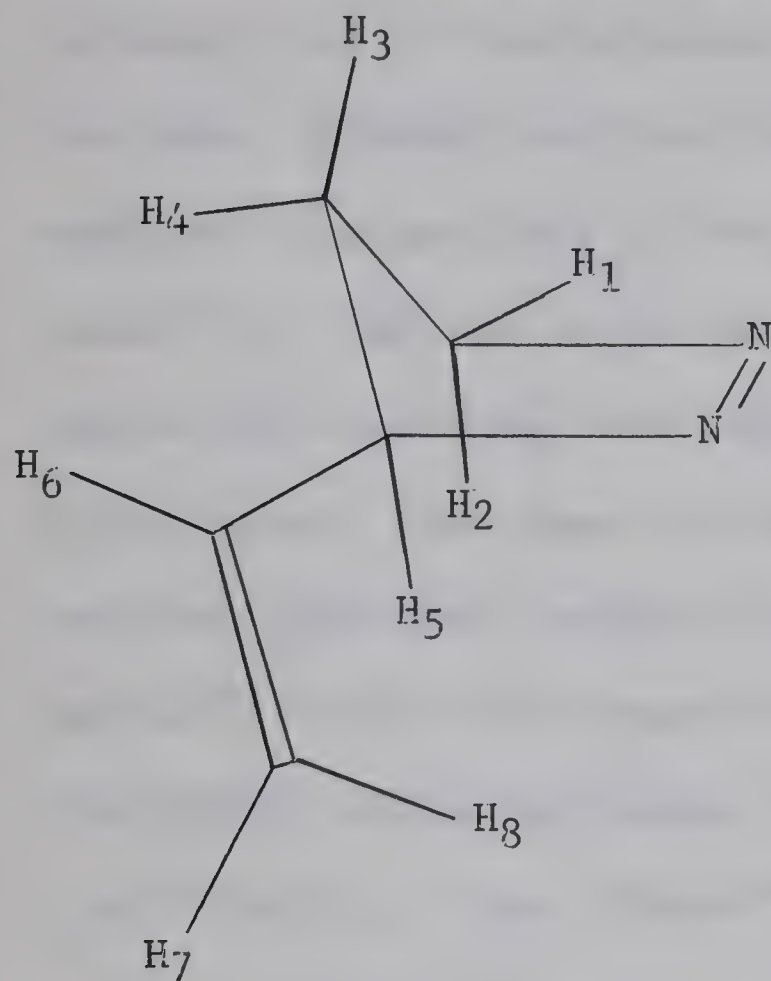


TABLE 5

THE NMR SPECTRUM OF 3-VINYLPYRAZOLINE (XXVI)



Coupling Constants (c.p.s.)

(Absolute Values)

$$J_{1,2} = 17.4$$

$$J_{1,3} = 9.7$$

$$J_{1,4} = 5.0$$

$$J_{1,5} = 2.3$$

$$J_{2,3} = 8.2$$

$$J_{2,4} = 9.0$$

$$J_{2,5} = 2.3$$

$$J_{3,4} = 12.6$$

$$J_{3,5} = 8.1$$

$$J_{4,5} = 8.8$$

$$J_{5,6} = 6.4$$

$$J_{5,7} = 1.4$$

$$J_{5,8} = 1.4$$

$$J_{6,7} = 10.0$$

$$J_{6,8} = 17.0$$

$$J_{7,8} = 1.7$$

Chemical Shifts (τ) (20% in CCl_4)

$$H_1 = 5.49$$

$$H_2 = 5.83$$

$$H_3 = 8.75$$

$$H_4 = 8.20$$

$$H_5 = 5.20$$

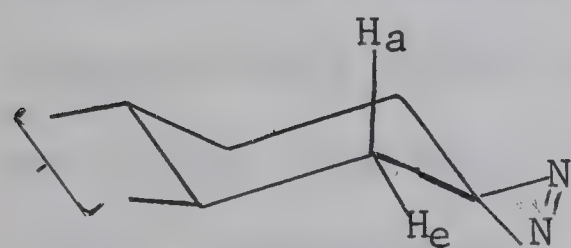
$$H_6 = 4.07$$

$$H_7 = 4.80$$

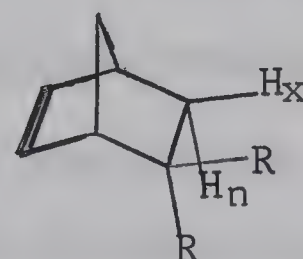
$$H_8 = 4.74$$

that XXVI exists in a similar conformation.

The chemical shift difference between the geminal protons is mainly due to the anisotropy of the nitrogen-nitrogen double bond. Mishra¹ ascribed the high-field proton at C₄ in puckered 1-pyrazolines to the proton furthest from the C₃C₅NN plane, i.e. the one in the axial position. It lies further inside the shielding zone, which is perpendicular to the C₃C₅NN plane, than does the equatorial proton. This assignment received additional support from the observation of Uebel and Martin³⁹ in the cyclohexane derivative containing a diazirine ring (XXX), where the signal due to H_e was observed at higher field than H_a. Also, Fraser⁴⁰ found considerable difference



XXX



XXXI

between the chemical shifts of the exo-proton (H_x) and the endo-proton (H_n) in norbornene compounds (XXXI). He assigned the lower-field proton to H_x which is nearer the plane of the double bond, while the higher-field proton was assigned to H_n which is in the shielding zone. The methylene protons at C₇ also experienced the same type of shielding.

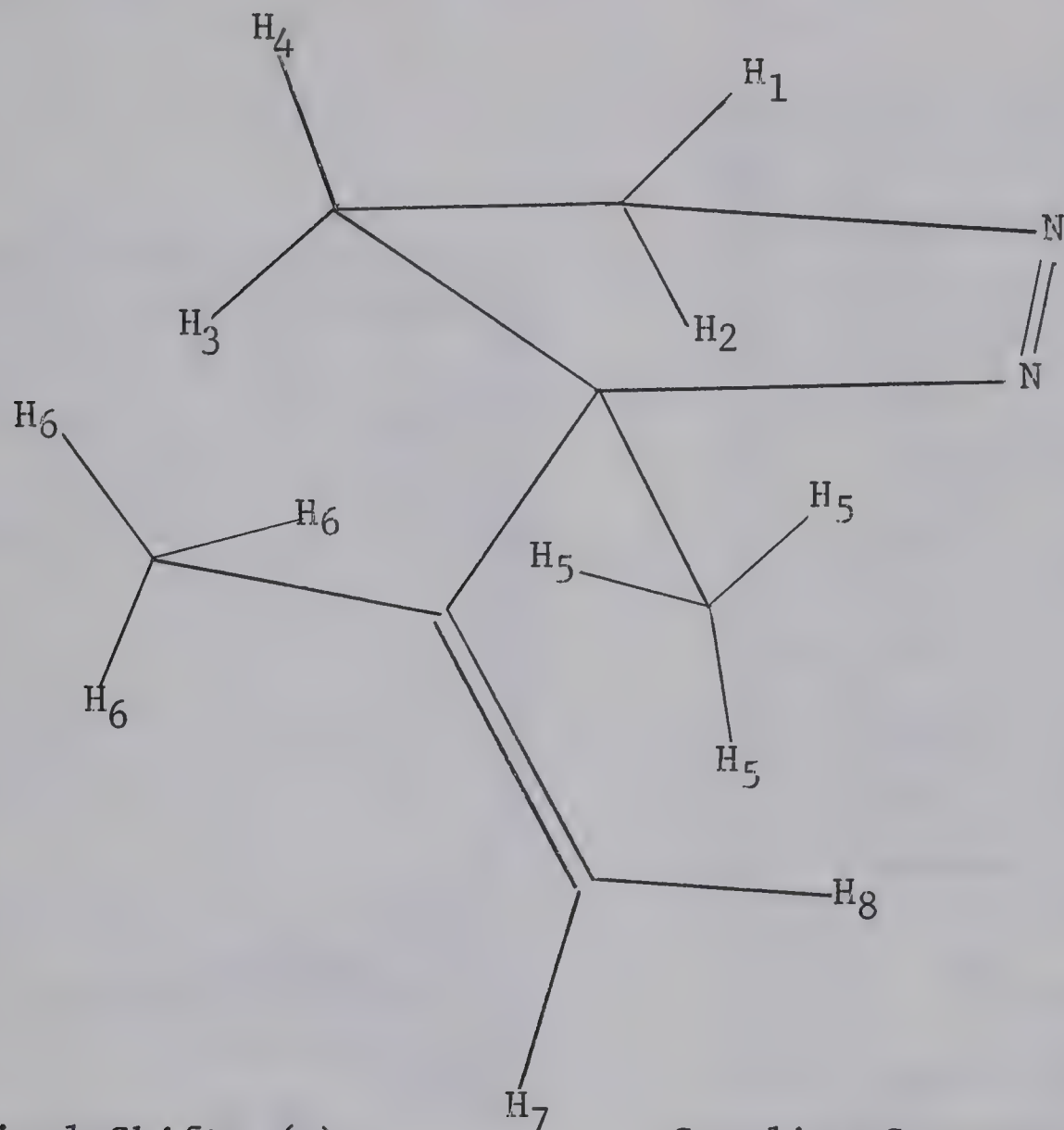
The structure of XXVII, prepared by the addition of diazomethane to 2,3-dimethylbutadiene, was confirmed in the

following manner. The microanalysis is consistent with a compound, $C_7H_{12}N_2$. The ultraviolet spectrum has a λ_{\max} at 324 m μ ($\epsilon=148$) in ethanol typical of 1-pyrazolines. There is no absorption above 3100 cm^{-1} in the infrared (Figure 4) indicative of the absence of nitrogen-hydrogen bonds in the molecule. The absorption at 1653 cm^{-1} is consistent with a carbon double bond carbon stretching mode. The A-60 nmr spectrum (Figure 7) has multiplets at τ 5.17, 5.63, 8.25, and 8.45 and a sharp singlet at τ 8.70 with integration ratios of 2:2:3:2:3 respectively, also consistent with structure XXVII. From the HA-100 spectrum with the help of decoupling techniques it is possible to get all of the chemical shifts and coupling constants, as shown in Table 6. Since the chemical shift differences between the geminal protons on C_4 and C_5 are very small the molecule has on the average, a near planar configuration. In other words the conformation where the methyl group is axial and the isopropenyl group equatorial has about the same population as the conformation where the isopropenyl group is axial and the methyl group equatorial.

3-Vinyl-1-pyrazoline-5,5- d_2 (XXXII) was prepared by the addition of diazomethane- d_2 to butadiene in ether solution. The diazomethane- d_2 was obtained by base catalyzed exchange of the protons of diazomethane with deuterium oxide. After three successive exchanges were carried out on the ether

TABLE 6

THE NMR SPECTRUM OF 3-METHYL-3-ISOPROPENYL-1-PYRAZOLINE



Chemical Shifts (τ)

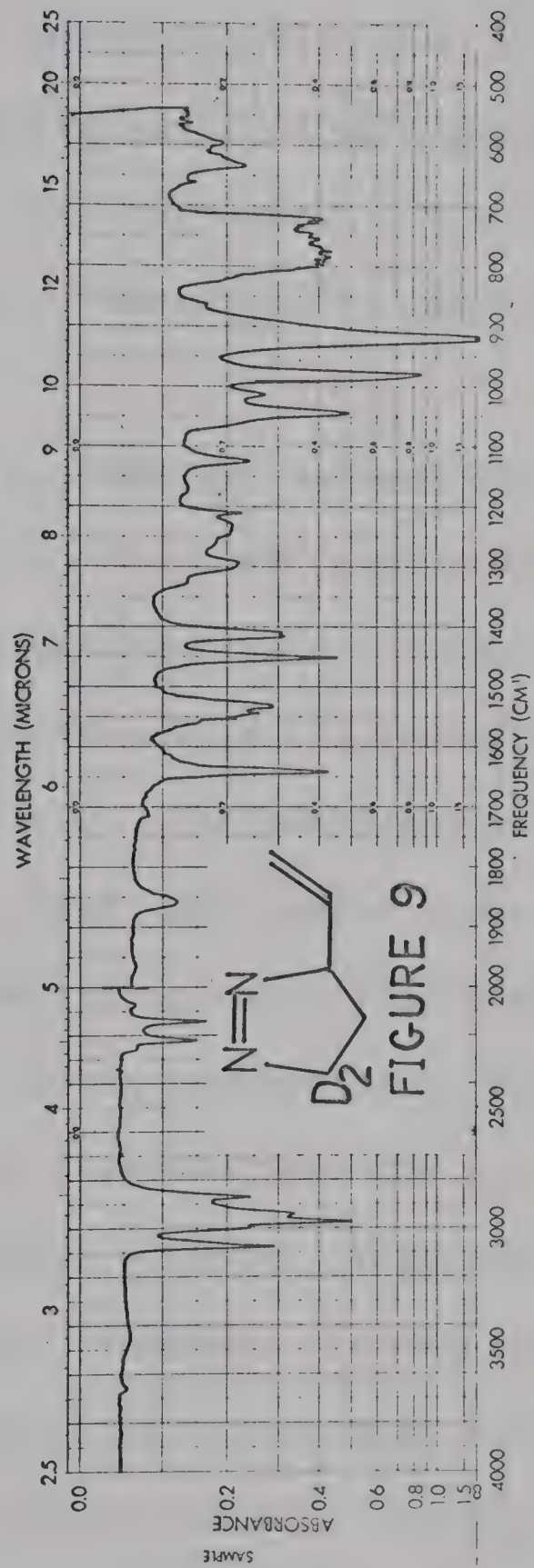
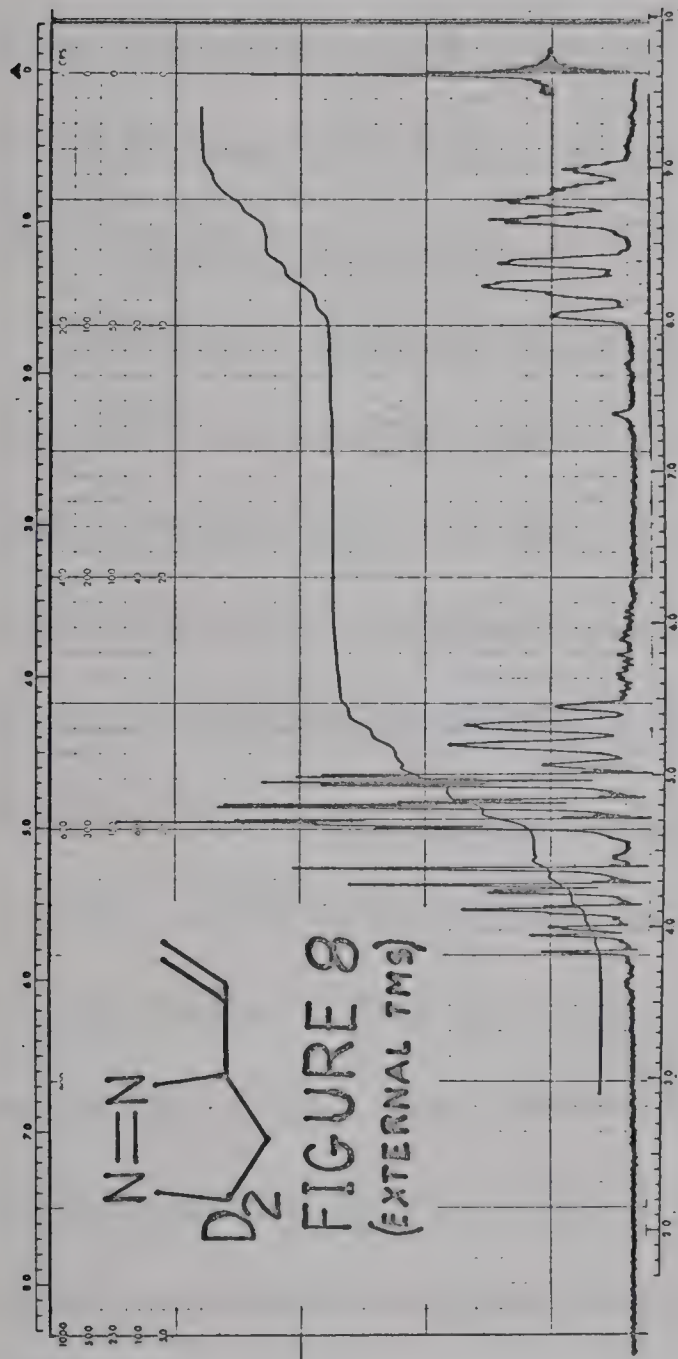
(Neat Liquid)

H ₁	=	5.625
H ₂	=	5.64
H ₃	=	8.66
H ₄	=	8.45
H ₅	=	8.70
H ₆	=	8.25
H ₇	=	5.20
H ₈	=	5.13

Coupling Constants (c.p.s.)

(Absolute Values)

J _{1,2}	=	17-18
J _{1,3}	=	6.9
J _{1,4}	=	8.6
J _{2,3}	=	7.8
J _{2,4}	=	7.8
J _{3,4}	=	12.5
J _{6,7}	=	1.4
J _{6,8}	=	0.8
J _{7,8}	=	1.4

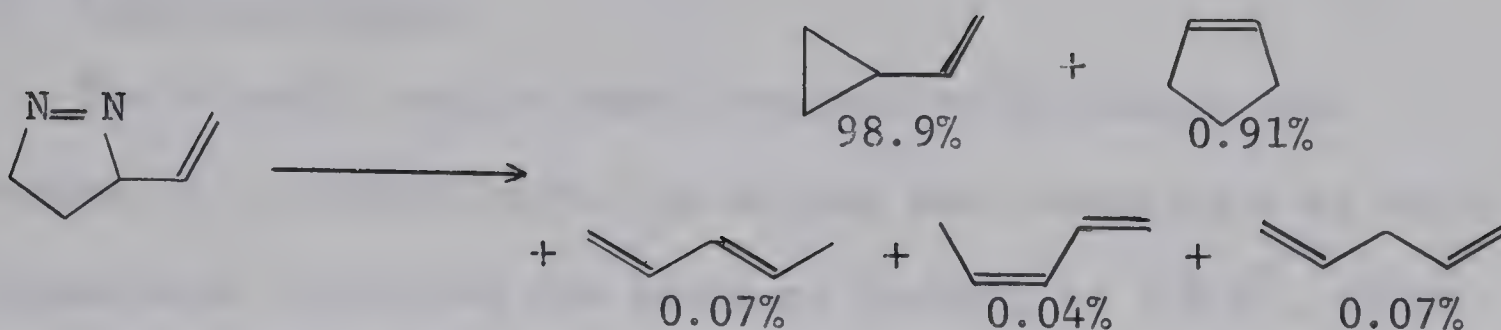


solution of diazomethane at 0°C, deuterium was incorporated into the molecule to the extent of 92-98%. An nmr spectrum of XXXII showed that the multiplet from τ 5.5-6.2 almost completely disappeared (Figure 8) indicating that the deuterium was incorporated into the C₅ position as expected. Also the multiplets at τ 8.20 and τ 8.75 decreased from a total of 24 lines to 8 lines if coupling by deuterium is neglected.

(B) Product Analysis

Kinetic studies were carried out on XXVI between 128° and 148° in the gas phase in a stainless steel reactor at pressures of 100-200 Torr. The product analysis was usually carried out on samples that were condensed in the vacuum rack by liquid nitrogen after a kinetic run. The samples were isolated in small glass ampoules, which were sealed under vacuum, and kept until it was necessary to break them open for analysis. The boiling points of the products were high enough to allow them to be injected directly into the gas chromatograph (g.c.) with a microliter syringe. The other technique that was used occasionally involved thermolysis of the pyrazoline in small glass bulbs at the desired temperature. Injection into the g.c. was attained by crushing the bulbs with a special "bulb crusher" which was built into the carrier gas stream.¹

Analysis of the hydrocarbon products shows that vinyl-



cyclopropane (98.9%) is the major product with small amounts of cyclopentene (0.91%), 1,4-pentadiene (0.07%), trans-1,3-pentadiene (0.07%) and cis-1,3-pentadiene (0.04%). The yields of these products were found to be reproducible throughout the temperature range of the kinetic study, i.e. 128-148°. All products were identified by comparison of their retention times on three columns with those of known samples. The vinylcyclopropane and cyclopentene peaks were further confirmed by nmr after they were trapped by preparative g.c..

The best g.c. column for the product analysis was found to be β,β -oxydipropionitrile on Chromosorb W ($\frac{1}{4}$ " X 20'), upon which complete separation of all of the products was possible at 0°. The two other columns that were used were squalene on Chromosorb P ($\frac{1}{4}$ " X 20') at 65° and dimethylsulfolane on Chromosorb W ($\frac{1}{4}$ " X 10') at 0°. However, trans-1,3-pentadiene could not be separated from vinylcyclopropane on the squalene column and cis-1,3-pentadiene had the same retention time as vinylcyclopropane on the dimethylsulfolane column.

(C) Kinetic Studies

The kinetic results were obtained by following the increase of pressure with time during the thermolysis of XXVI. A transducer converted the pressure reading to E.M.F., which was indicated on a strip chart recorder. Since the time (t) was also recorded it was possible to obtain a rate constant for every kinetic run. First order kinetics were observed to greater than 90% completion.

The rate constants were obtained from the data in the following manner. For a first order gas phase reaction of the type, $A \rightarrow \text{products}$, it can be shown⁴¹ that

$$2.303 \log \frac{(P_{\infty}^a - P_0^a)}{(P_{\infty}^a - P_t^a)} = kt \quad (1)$$

where P^a is the actual pressure inside the reactor; k is the first order rate constant and t is time. In the present case the measured pressure $P = P^a - P_x$, where P_x is the pressure to push the diaphragm against the needle.

$$\text{Therefore, } \log (P_{\infty} - P_t) = \frac{-kt}{2.303} + \text{const.} \quad (2)$$

It is known that in the pressure range used, the transducer E.M.F. (E), which is that recorded on the chart paper is directly proportional to P,

$$\text{i.e. } P = aE + b \quad (3)$$

where a and b are proportionality constants depending on the particular transducer.

$$\text{Therefore, } \log [aE_{\infty} + b - (aE_t + b)] = \frac{-kt}{2.303} + \text{const.} \quad (4)$$

$$\text{and } \log (E_{\infty} - E_t) = \frac{-kt}{2.303} + \text{const.} \quad (5)$$

A plot of $\log (E_{\infty} - E_t)$ against t gives $-k/2.303$ from which k is easily evaluated. An example of such a plot is shown in Figure 10.

Mishra¹ found that the error in the measurement of k is about 1% when only the error in the measurement of E is considered, and at most 2-3% when fluctuation of the reactor temperature is also considered. Since the same apparatus was used for thermolysis of XXVI the rate constants obtained are also expected to be reliable to 2-3%.

The effect of temperature on the rate constant is given by the Arrhenius equation (6),

$$k = A e^{-E_a/RT} \quad (6)$$

where E_a is the activation energy and A is the frequency factor. Equation 6 can also be expressed in the logarithmic forms, (7) and (8). The activation energy E_a was obtained from a slope of a plot of $\log k$ vs. $1/T$. Once E_a was found, $\log A$ was calculated from equation 8. Both parameters were also obtained by the method of least squares.

$$\ln k = \ln A - E_a/RT \quad (7)$$

$$\text{or } \log k = \log A - \left[\frac{E_a}{2.303R} \right] \left[\frac{1}{T} \right] \quad (8)$$

For a gas phase reaction

$$\Delta H^{\ddagger} = E_a - n R T \quad (9)$$

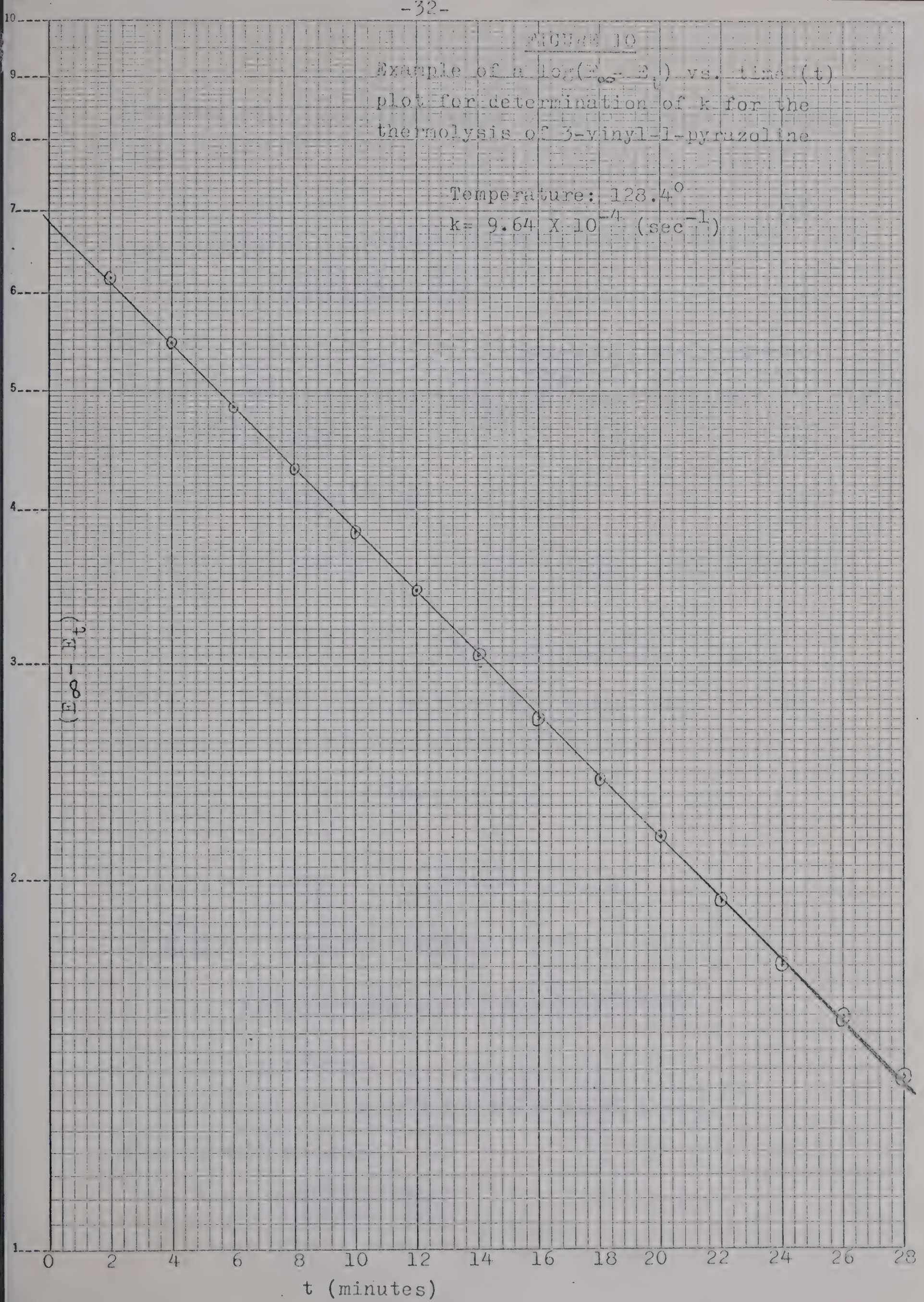
where ΔH^{\ddagger} is the enthalpy of activation and n is the order of

FIGURE 10

Example of a $\log(E_{\infty} - E_t)$ vs. time (t) plot for determination of k for the thermolysis of 3-vinyl-1-pyrazoline

Temperature: 128.4°

$k = 9.64 \times 10^{-4} \text{ (sec}^{-1}\text{)}$



the reaction. For a first order reaction equation 9 becomes equation 10.

$$\Delta H^\ddagger = E_a - RT \quad (10)$$

From transition state theory⁴¹

$$k = (k' T/h) e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R} \quad (11)$$

where k' is Boltzmann's constant and h is Plank's constant.

From 6, 10 and 11 an expression for ΔS^\ddagger can be obtained.

$$\Delta S^\ddagger = R \ln \frac{Ah}{k' T_e} \quad (12)$$

$$\text{or } \Delta S^\ddagger = 2.303R \left[\log \frac{h}{k' T_e} + \log A \right] \quad (13)$$

The entropy of activation was calculated at temperatures 250° and 135°.

The results of the kinetic experiments are shown in Table 7. Data for the least squares calculation⁴² of the activation parameters are shown in Table 8.

From the data in Table 8,

$$y = mx + b$$

$$\log k = \left[\frac{-E_a}{2.303 \times R \times 1000} \right] \left[\frac{1000}{T} \right] + \log A$$

$$\begin{aligned} \frac{-E_a}{2.303R} = m &= \frac{n \sum (xy) - \sum x \sum y}{n \sum x^2 - (\sum x)^2} \\ &= \frac{11(-69.462882) - (26.7237)(-28.5368)}{11(64.942442) - (26.7237)^2} \\ &= -7.036921 \end{aligned}$$

$$E_a = 7.036921 \times 2303 \times 1.987 = 32201.37 \text{ cal.}$$

$$= 32.2 \text{ k cal.}$$

$$\log A = b = \frac{\sum x^2 \sum y - \sum x \sum xy}{n \sum x^2 - (\sum x)^2}$$

TABLE 7

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE
THERMOLYSIS OF 3-VINYL-1-PYRAZOLINE (XXVI)

Run No.	Temperature (°C)	Rate Constant $10^4 k(\text{sec}^{-1})$	Activation Parameters
1	138.4	25.4	
2	139.6	27.7	
3	136.7	21.8	
4	135.75	19.7	$E_a = 32.2 \pm 0.2 \text{ kcal.}$
5	131.75	13.25	$\log A = 14.5$
6	128.4	9.64	$\Delta S_{250}^\ddagger = 4.7 \text{ e.u.}$
7	128.0	9.11	$\Delta S_{135}^\ddagger = 5.2 \text{ e.u.}$
8	147.6	61.0	
9	148.5	60.8	
10	146.9	55.3	
11	143.5	40.2	

TABLE 8

LEAST SQUARES CALCULATION OF THE ACTIVATION PARAMETERS FOR THE THERMOLYSIS OF

3-VINYL-1-PYRAZOLINE

Run No.	y ($\log_{10} k$)	x ($1000/T$)	x^2	xy	$(mx+b-y)$	$10^8 (mx+b-y)^2$
9	-2.2161	2.3720	5.626384	-5.256589	+0.0259	67081
8	-2.2147	2.3770	5.650129	-5.264342	-0.0106	11236
10	-2.2573	2.3810	5.669161	-5.374631	+0.0035	1225
11	-2.3958	2.4004	5.761920	-5.750878	+0.0058	3364
2	-2.5575	2.4230	5.870929	-6.196822	+0.0085	7225
1	-2.5952	2.4300	5.804900	-6.306336	+0.0025	625
3	-2.6615	2.4403	5.955064	-6.494858	-0.0093	8649
4	-2.7055	2.4456	5.981937	-6.617112	-0.0026	676
5	-2.8778	2.4702	6.101888	-7.108741	-0.0034	1156
6	-3.0159	2.4910	6.205081	-7.512607	-0.0116	13456
7	-3.0405	2.4930	6.215049	-7.479966	-0.0011	121
Σ	= -28.5368	26.7237	64.942442	-69.462882		114814

1
35
1

$$= \frac{(64.942442)(-28.5368) - (26.7237)(-69.462882)}{-0.21072}$$

$$= 14.501427 \text{ or } 14.50$$

The Arrhenius equation for thermolysis of XXVI therefore becomes

$$k = 10^{14.50} e^{(-32.2/RT)}$$

$$\Delta S_{250}^{\ddagger} = 2.303R \log \frac{Ah}{k^{\ddagger} T_e}$$

$$= 4.57 (\log A - 13.472)$$

$$= 4.57 (14.50 - 13.472)$$

$$= 4.70 \text{ e.u.}$$

$$\Delta S_{135}^{\ddagger} = 4.57 (14.50 - 13.364)$$

$$= 5.19 \text{ e.u.}$$

The probable error in the slope⁴³ (P_m) is given by

$$P_m = P_y \sqrt{\frac{n}{n \sum x^2 - (\sum x)^2}}$$

where P_y is the probable error of the residuals.

$$P_y = 0.6745 \sqrt{\frac{\sum (mx+b-y)^2}{n-2}}$$

$$P_y = 0.6745 \sqrt{\frac{1.1481 \times 10^{-3}}{9}}$$

$$= 0.00761$$

$$P_m = 0.00761 \sqrt{\frac{11}{0.21072}}$$

$$= 0.0550$$

The error in the activation energy E_a in kcal /mole can now be calculated.

$$\text{Error} = 0.0550 \times 2.303 \times 1.987 = 0.252 \text{ kcal.}$$

$$E_a = 32.2 \pm 0.25 \text{ kcal./mole}$$

The probable error of the intercept⁴³ (P_b) is given by

$$\begin{aligned} P_b &= P_y \sqrt{\frac{\sum x^2}{n \sum x^2 - (\sum x)^2}} \\ &= 0.00761 \sqrt{\frac{64.942}{0.21072}} \\ &= 0.1335 \end{aligned}$$

$$\log A = b = 14.50 \pm 0.13$$

$$\text{and } \Delta S_{250}^\ddagger = +4.7 \pm 0.5 \text{ e.u.}$$

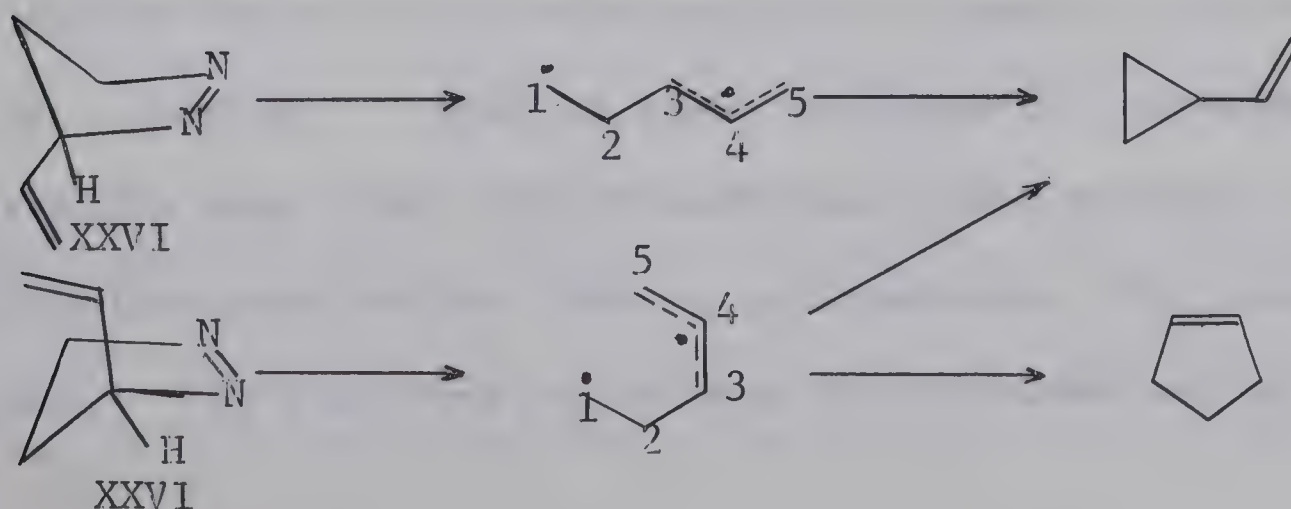
$$\Delta S_{135}^\ddagger = +5.2 \pm 0.5 \text{ e.u.}$$

(D) Mechanism

As was stated in the historical section, Mishra¹ and Erickson⁸ obtained good evidence for a hydrocarbon intermediate during the thermolysis of alkyl-1-pyrazolines. The intermediate was found to be symmetrical and to have the properties of a " π -cyclopropane." Because XXVI is a similar compound, it is expected to have a similar mechanism of thermolysis. The observed activation energy (32.2 kcal) represents a decrease of 10.2 kcal from that of 1-pyrazoline (I) (42.4 kcal). The decrease is attributed to a contribution from the allylic resonance energy, which stabilizes the transition state. There is some doubt as to the correct value of the resonance energy of the allyl radical. Theoretical estimates⁴⁴ and early experimentally based estimates^{45,46} predict a value of 15-18 kcal. More recently, Benson⁴⁷ and Frey²⁹ have suggested the smaller

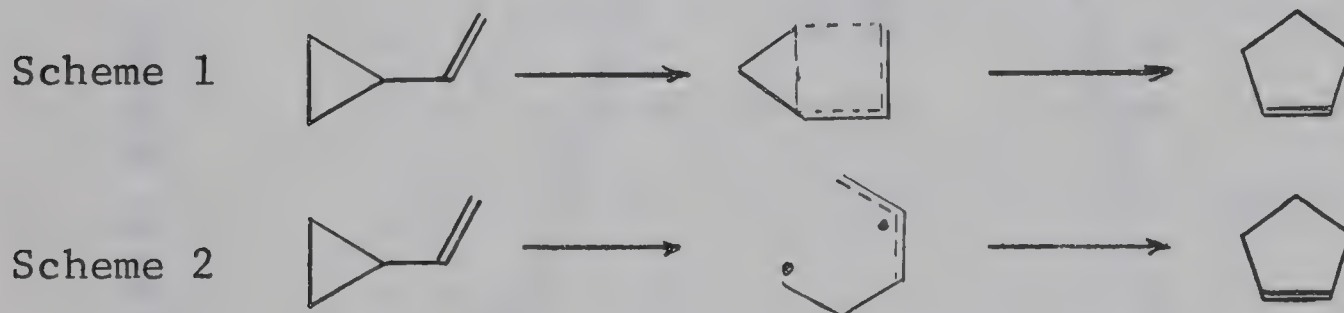
values of 13 ± 1 and 12 ± 1 kcal. respectively. The value of 10.2 kcal. for the allylic resonance energy contribution to the thermolysis of XXVI suggests that the electron is nearly completely delocalized in the rate determining transition state if Frey and Benson's estimates are correct. Of course, if the earlier estimates are closer to the true value then the value of 10.2 kcal. implies that the C₃-N bond is only 55-65% broken in the rate determining transition state, similar to what Seltzer suggests from secondary kinetic isotope effect data in various azo compounds.¹⁴

The product proportions support the suggestion that the intermediate is a " π -cyclopropane" in that it prefers to undergo 1,3-closure to form vinylcyclopropane rather than 1,5-closure to form the more thermodynamically stable cyclopentene. Since XXVI is expected to decompose with the vinyl group in the equatorial position the intermediate produced would be in the trans- configuration. In order for 1,5-closure to occur the intermediate has to rotate into a suitable position. This rotation is expected to be hindered



by partial bonding between C₁ and C₃ as well as by the delocalization energy of the allylic radical, so it is likely that the small amount of cyclopentene that is formed arises from the cisoid intermediate that is obtained when XXVI is thermolyzed with the vinyl group in the axial position. In this case the geometry would be much more favorable for 1,5-closure.

It is interesting to speculate as to the similarities of the intermediates involved in the thermolysis of XXVI and the vinylcyclopropane isomerization to cyclopentene. From the present work it is still impossible to rule out the concerted mechanism (Scheme 1), however it does show that cyclopentene can be formed from a vinyltrimethylene

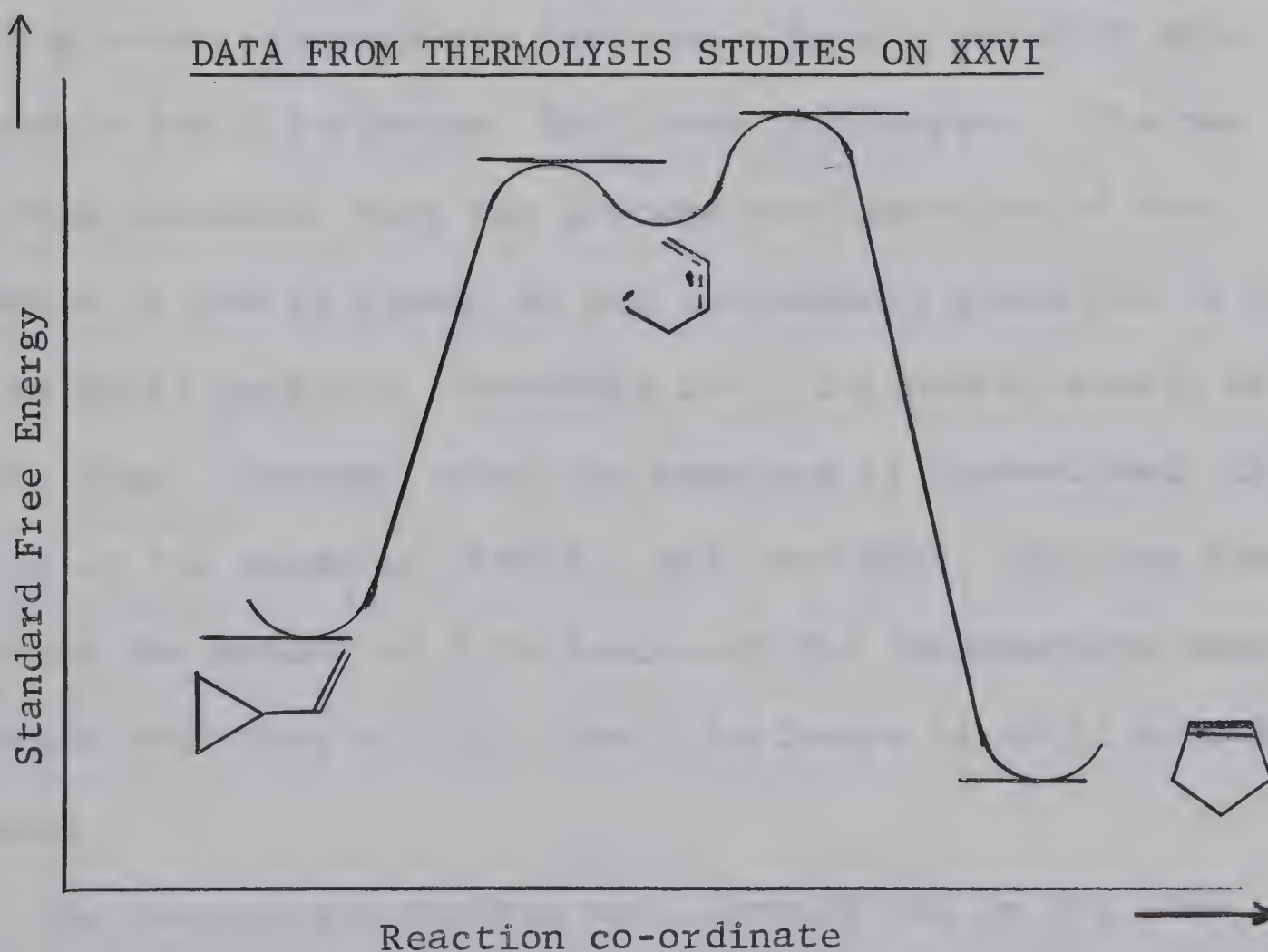


intermediate such as predicted by Scheme 2. If a vinyltrimethylene species is involved as an intermediate in the vinylcyclopropane to cyclopentene rearrangement, then an energy diagram such as shown in Figure 11 is suggested. Our results show that vinyltrimethylene prefers to go to vinylcyclopropane rather than to cyclopentene. The energy diagram is also consistent with the observations of cis-

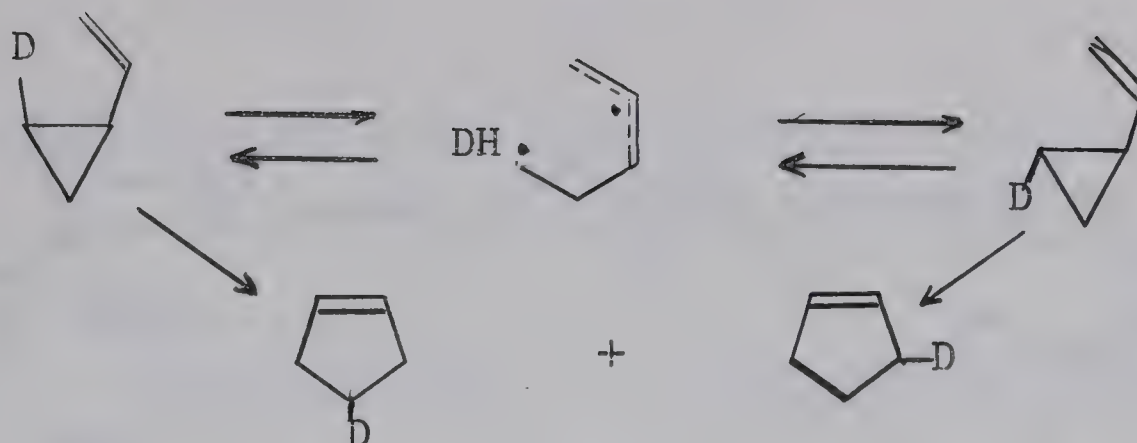
trans isomerizations of various 1,2-disubstituted cyclopropanes²⁴ and with the isomerization of trans-1-methyl-2-vinylcyclopropane to its cis-isomer,²⁹ which immediately decomposes to cis-1,4-hexadiene. In the latter reaction no 4-methylcyclopentene was found, which means that less energy is required for the cis-trans isomerization as suggested by the reaction co-ordinate in Figure 11.

FIGURE 11

REACTION CO-ORDINATE FOR THE VINYL CYCLOPROPANE TO
CYCLOPENTENE REARRANGEMENT AS SUGGESTED BY
DATA FROM THERMOLYSIS STUDIES ON XXVI



Further evidence for a reaction co-ordinate such as shown in Figure 11 has very recently been obtained by Willcott and Cargle.⁴⁸ They found that, during the first 6% of the

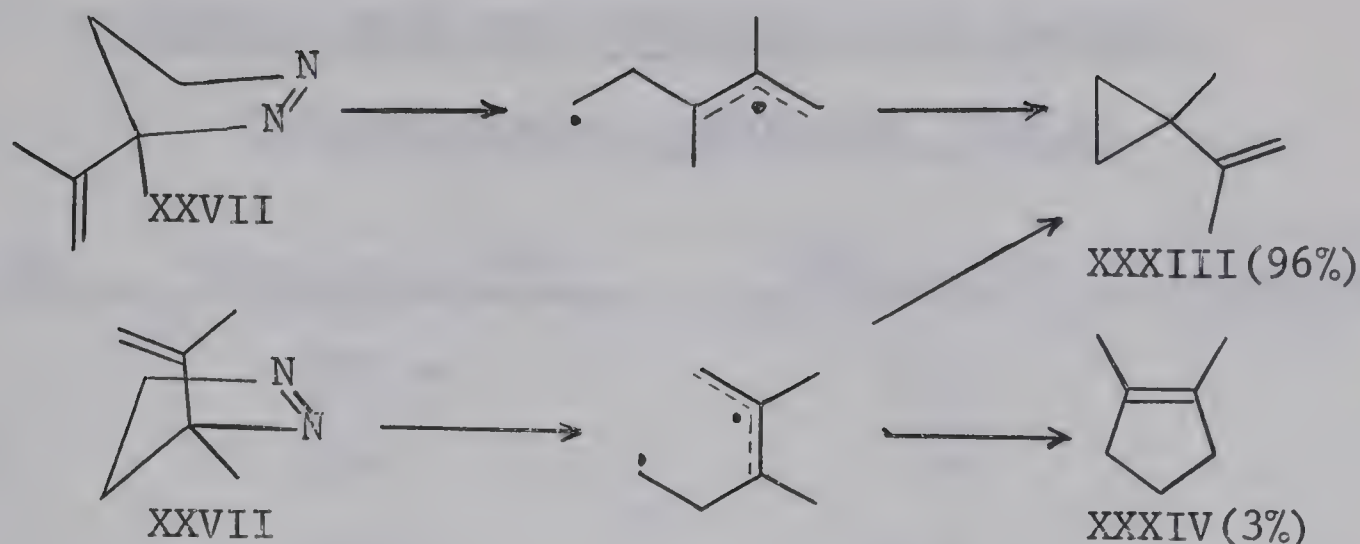


irreversible isomerization of cis- or trans-2-deuterio-vinylcyclopropane to cyclopentene, complete loss of stereochemistry at the labeled site occurs.

(E) Thermolysis of 3-Methyl-3-isopropenyl-1-pyrazoline (XXVII)

In order to obtain a vinylpyrazoline which upon thermolysis would give an intermediate that would have a geometry more favorable for 1,5-closure, XXVII was synthesized. The nmr spectrum indicates that the average configuration of the molecule is nearly planar so the isopropenyl group has to be in the axial position, favorable for 1,5-closure, nearly half of the time. However, when the compound is thermolyzed, the yields of the products (XXXIII, 96%; and XXIV, 3%) show that although the amount of 1,5-closure of the intermediate does increase over that of XXVI, the 1,3-closure is still greatly favored.

The thermolysis studies were carried out in the same reactor and at nearly the same rates as XXVI. The rate of thermolysis of XXVII was found to be 0.30 times that of XXVI due to an increase of 1.4 kcal. in the activation energy.



It is interesting to compare the activation energies for thermolysis of XXVI and XXVII (32.2 and 33.6 kcal. resp.) with those for the isomerization of vinylcyclopropane²⁵ and 1-methyl-1-isopropenylcyclopropane⁴⁹ (49.6 and 50.5 kcal. resp.). The similar increase observed in the activation energies of the two reactions upon the addition of two methyl groups indicates that the methyl groups affect the reaction co-ordinate in a similar manner. The effect is possibly due to a slight steric hindrance making it more difficult for the molecule to attain a position where the maximum benefit from allylic resonance can be obtained in the transition state.

TABLE 9

RELATIVE RATES OF THERMOLYSIS OF 3-VINYL-1-PYRAZOLINE (XXVI)
AND 3-METHYL-3-ISOPROPENYL-1-PYRAZOLINE (XXVII) at 142.4°C

Compound	$10^4 k(\text{sec}^{-1})$	Relative Rate
3-vinyl-1-pyrazoline (XXVI)	36.3	1.00
3-methyl-3-isopropenyl-1-pyrazoline (XXVII)	10.3	0.30

TABLE 10

KINETIC DATA FROM THERMOLYSIS OF 3-METHYL-

3-ISOPROPENYL-1-PYRAZOLINE (XXVII)

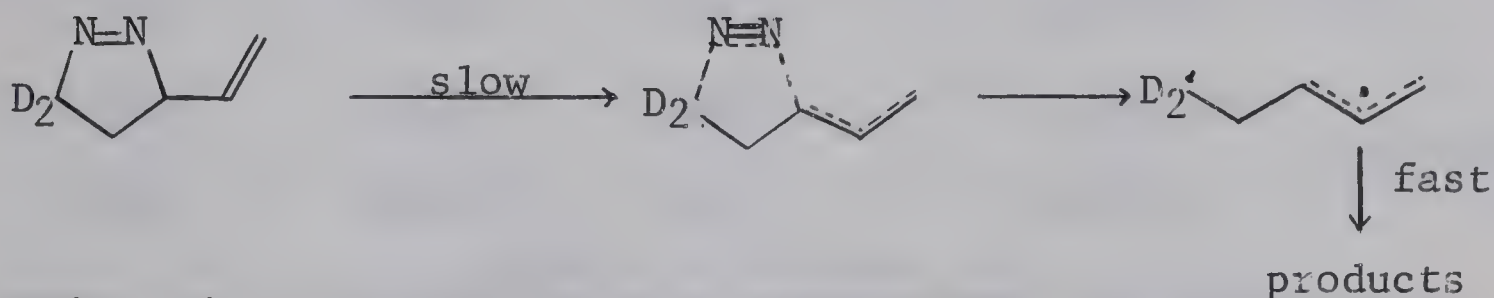
Run No.	Temperature(°C)	$10^4k(\text{sec}^{-1})$	Activation Parameters
1	139.44	8.13	
2	139.3	7.94	
3	142.4	10.8	
4	147.9	18.6	$E_a=33.6\pm0.3 \text{ kcal}$
5	151.0	24.2	$\text{Log } A=14.7\pm0.2$
6	154.5	33.6	$\Delta S_{250}^\ddagger=5.6\pm0.7 \text{ e.u.}$
7	154.7	34.9	
8	155.15	36.9	

(F) Thermolysis of 3-Vinyl-1-pyrazoline-5,5-d₂ (XXXII)

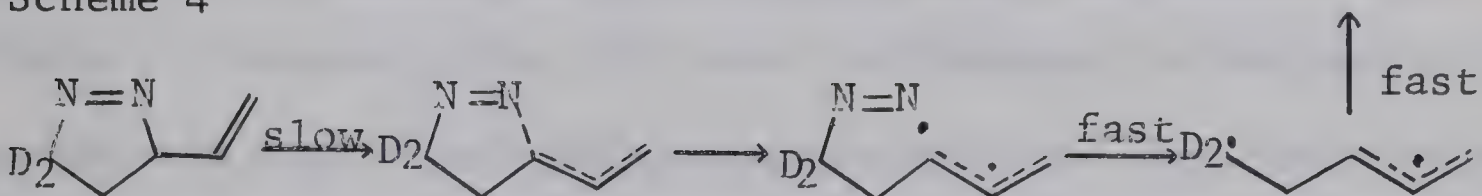
Mishra,^{1,3,5} from observations on rates of thermolysis of alkyl-1-pyrazolines, suggested that both carbon-nitrogen bonds were breaking simultaneously in the rate-controlling step. Seltzer has used secondary kinetic isotope effects as a means of determining the amount of bond breaking that occurs in the slow step of the thermolysis of various azo-compounds.¹¹⁻¹⁴ He found a secondary kinetic isotope effect of 12-15% per deuterium atom when the deuterated carbon undergoes a hybridization change on going from the starting state to the transition state. When the CD-N bond cleaves in a subsequent fast step, no isotope effect is observed.

In order to determine whether the cleavage of both carbon-nitrogen bonds (Scheme 3) occurs in the rate determining step during the thermolysis of XXVI, 3-vinyl-1-pyrazoline-5,5-d₂ (XXXII) was prepared. The other possibility (Scheme 4) involves cleavage of only the C₃-N

Scheme 3



Scheme 4



bond in the rate determining step with the C₅-N bond breaking in a subsequent fast step. No isotope effect would be expected if the thermolysis proceeds through Scheme 4.

Upon thermolysis a secondary kinetic isotope effect was indeed observed (Table 11). It, $k_H/k_D = 1.21 \pm 0.03$, is only slightly lower than the 12-15% per deuterium atom observed by Seltzer on various azo compounds under slightly different conditions. Therefore, a considerable amount of hybridization change occurs at C₅ between the starting state and the transition state which means that the C₅-N bond breaks in the rate determining step as suggested by

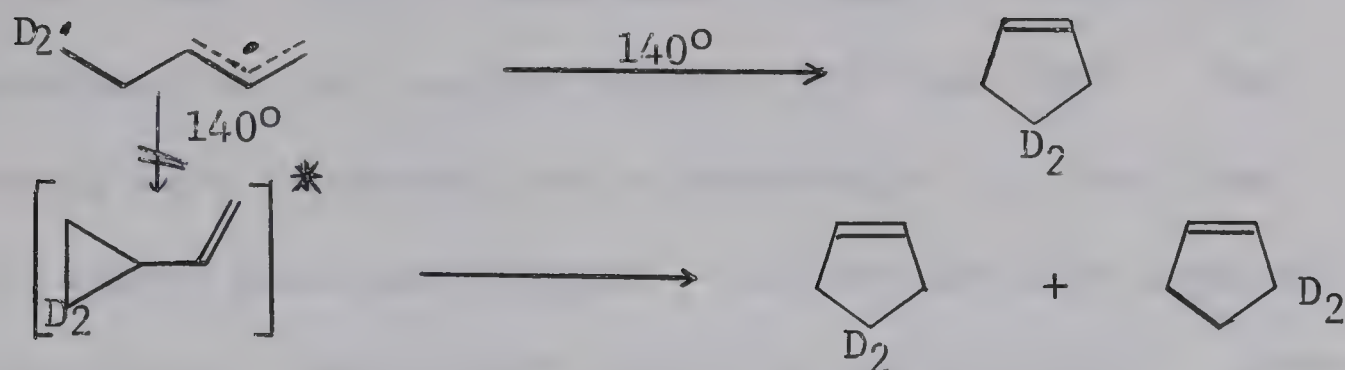
TABLE II

THE SECONDARY KINETIC ISOTOPE EFFECT FOR THE
THERMOLYSIS OF 3-VINYL-1-PYRAZOLINES-5,5-d₂ (XXXII)

Experiment	Compound	Temperature (°C)	$10^4 k (\text{sec}^{-1})$	k_H/k_D
1 (a)	XXVI	134.4	17.2 ± 0.2	1.22 ± 0.03
1 (b)	XXXII	134.4	14.1 ± 0.2	
2 (a)	XXVI	135.5	17.5 ± 0.2	1.20 ± 0.03
2 (b)	XXXII	135.5	14.6 ± 0.2	
$k_H/k_D = 1.21 \pm 0.03$				

Scheme 3. However, the 10.2 kcal. difference in the activation energies between I and XXVI suggests that the C₃-N bond breaks easier than the C₅-N bond. In order to explain both observations we believe that both bonds are breaking in the rate-determining step, but that this cleavage is not symmetrical, the amount of C₃-N bond breaking being greater than that of the C₅-N bond.

The small amount of cyclopentene produced by thermolysis of XXXII at 140° was trapped by preparative g.c. and its nmr spectrum was taken in order to determine whether it arose directly from the intermediate or from a small amount of decomposition of a "hot" vinylcyclopropane intermediate. The spectrum consisted of two singlets at τ 4.38 and τ 7.73 at an intensity ratio of 1:2. The resonance at τ 7.73 (a triplet in the non-deuterated cyclopentene) is a broad singlet as expected when C₄ is deuterated. Since there is



no resonance at $\gamma_{8.2}$ all of the deuterium has to be at C_4 . If the cyclopentene arises from a "hot" vinylcyclopropane the deuterium would be observed at both C_3 and C_4 ; therefore it must arise directly from the vinyltrimethylene intermediate.

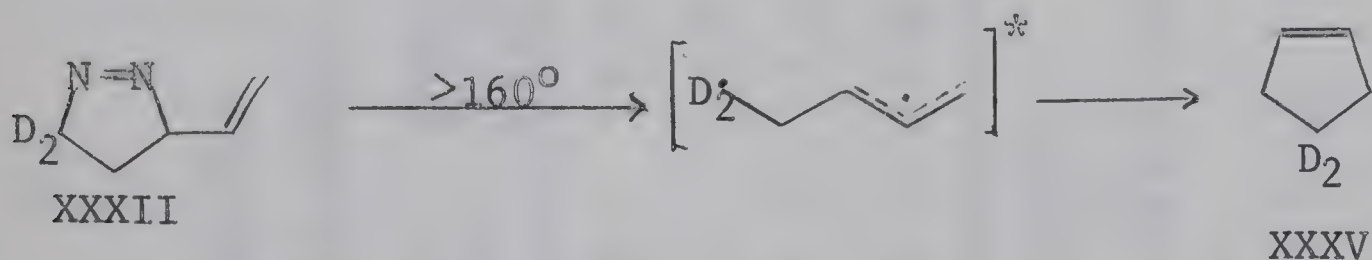
(G) Effect of Temperature on Product Proportions

Analysis of the products of the kinetic runs between 128° and 148° indicated that the yields were reproducible. However, when XXVI was thermolyzed in the injection port of the g.c. at temperatures $>200^\circ$ the yields of cyclopentene and the pentadienes were observed to have increased at the expense of vinylcyclopropane. Two new products, butadiene and cyclopentadiene, were also observed. In order to examine the effect of temperature on the product proportions, a series of thermolyses were carried out in the reactor at temperatures ranging between 128° and 186° . The data, together with the estimated half lives of XXVI at the various temperatures is shown in Table 12. The results show that the abnormal product proportions begin at 160° and increase at higher temperatures.

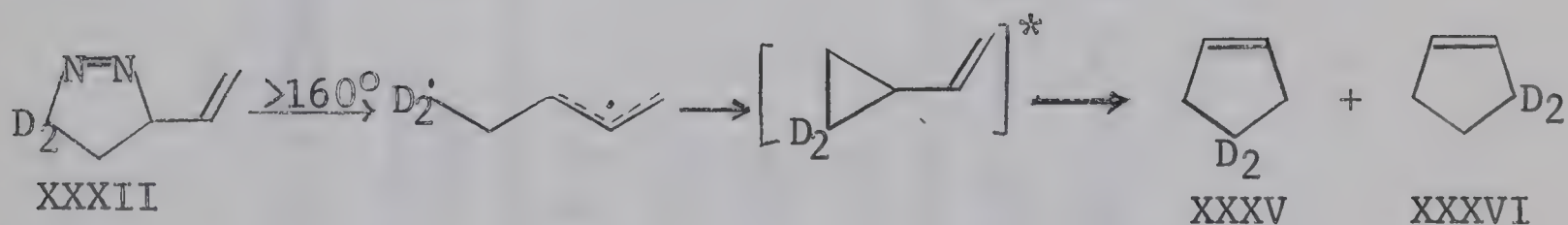
In order to determine whether the abnormal amount of cyclopentene arises directly from the intermediate (Scheme 5)

or via a "hot" vinylcyclopropane (Scheme 6), XXXII was thermolyzed in the reactor between 175° and 180° . The products were injected into a preparative g.c. and the cyclopentene peak was trapped. Its nmr spectrum indicated the product ratio (XXXV:XXXVI) to be $47 \pm 3 : 53 \pm 3$. Therefore, a "hot" vinylcyclopropane must be a precursor as predicted by Scheme 6. As a control experiment both cyclopentene and vinylcyclopropane were recovered unchanged after one hour at 180° in the reactor.

Scheme 5



Scheme 6



At the higher temperatures a rather high yield of cyclopentadiene was observed indicating that the cyclopentene was also vibrationally excited when formed from the "hot" vinylcyclopropane. Cyclopentadiene was also observed by Frey³¹ as a product of the addition of methylene to butadiene at low pressures. Analysis of the light gases from the thermolysis of XXXII at 186° showed H_2 (58.5%),

TABLE 12

EFFECT OF TEMPERATURE ON PRODUCT PROPORTIONS^b

Temp. (°C)	t _{1/2} (sec)	butadiene	1,4-penta- diene	cyclo- pentene	trans- 1,3-pent- adiene	cis- 1,3-pent- adiene	vinyl- cyclo- propane	cyclo- pentadiene
128.4	720	nil	0.07	0.91	0.07	0.04	98.91	nil
160	40 ^a	nil	0.25	1.7	0.25	0.1	97.5	0.3
172	14 ^a	0.72	3.8	20.8	3.25	2.0	62.0	7.5
186	4.7 ^a	2.2	5.5	29.8	8.0	4.4	21.4	29.3

(a) Obtained by extrapolation from lower temperature.

(b) A ¼" X 20' β,β-oxydipropionitrile on chromosorb W column was used for the analysis.

HD(40.8%), and D₂(0.8%). The possibility also exists that some of the vinylcyclopropane produced at the higher temperatures has already made the trip to cyclopentene and back; if so some deuterium should be observed in the terminal methylene of the vinyl group. A nmr spectrum (100 Mc) of a sample of vinylcyclopropane that was isolated from the products of thermolysis of XXXII at 181° showed that the integrated intensities of the terminal methylene was exactly twice that of the other proton in the vinyl group; therefore it contained no deuterium and no vinylcyclopropane arises from a "hot" cyclopentene.

From the heats of formation and activation energy data^{25,50} construction of an energy diagram for the various reactions observed at temperatures above 160°C was possible (Figure 12). The heat of formation of XXVI was estimated by adding the difference between the heats of formation of azomethane and trans-2-butene (+43.2 and -2.18 kcal. mole⁻¹ respectively) to the value estimated for vinylcyclopentene (+23.2 kcal. mole⁻¹). The estimates for vinylcyclopentene and vinylcyclopropane were obtained by the method of Janz,⁵¹ which involved the use of group additivities. The heats of formation of cyclopentene⁵¹ (+8.18 kcal. mole⁻¹) and cyclopentadiene⁵³ (+31.8 kcal. mole⁻¹) are known precisely. The estimated values⁵⁴ are expected to be accurate to within ±2 kcal. mole⁻¹, however

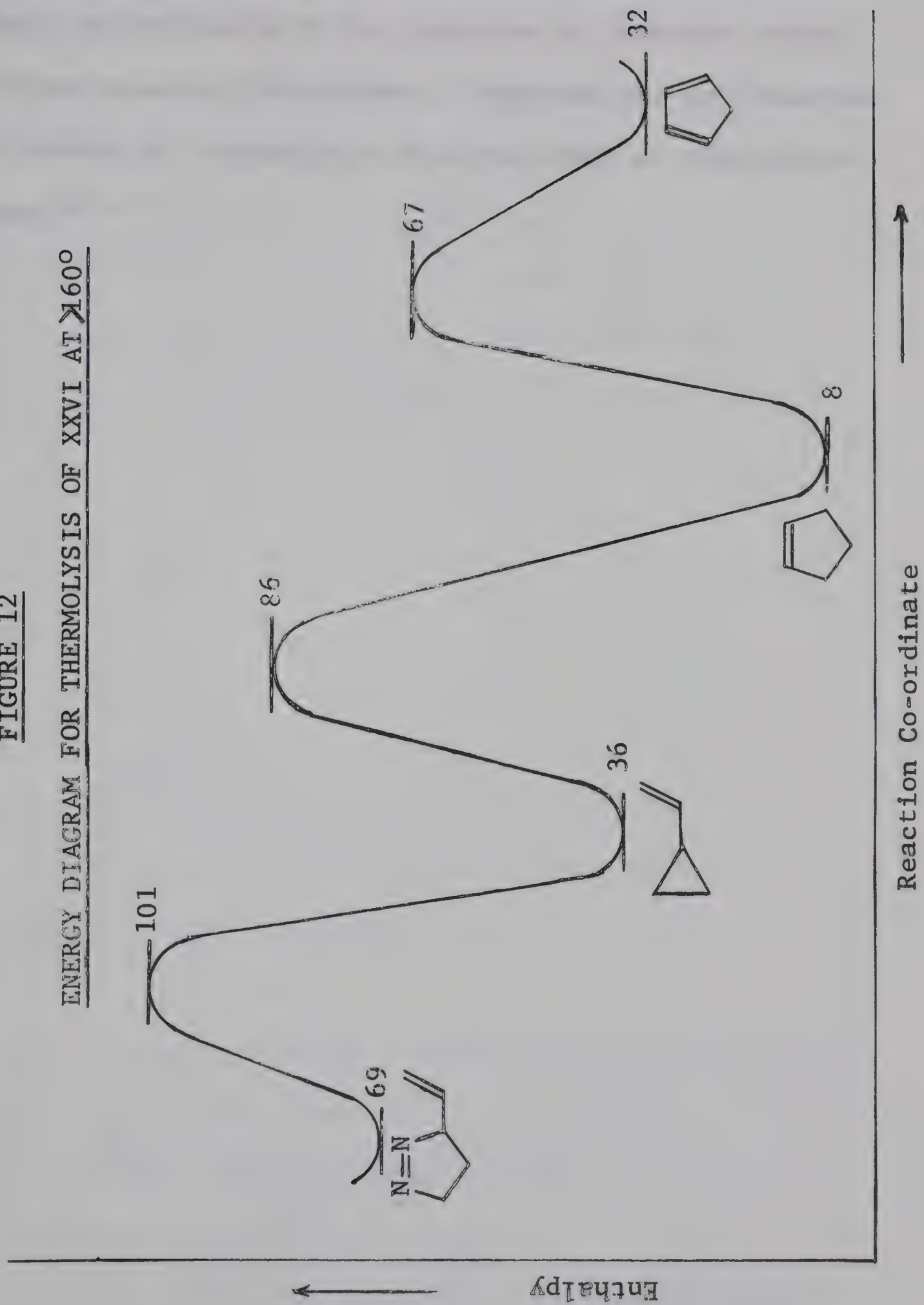
Figure 12 shows that even much larger error would not affect the conclusions.

The transition state of the thermolysis reaction of XXVI has a much higher energy than that of the subsequent processes (Figure 12), so the initially formed vinylcyclopropane is expected to be vibrationally excited.⁵⁴ Evidently, at temperatures below 160° and at the pressures used (100-200 Torr) collisional deactivation is efficient in allowing all of the vibrationally excited species to be deactivated to vinylcyclopropane. As stated earlier, a control experiment showed that the small amount of cyclopentene that does form at the lower temperature (135°) arises directly from the intermediate and not via a "hot" vinylcyclopropane. However, at temperatures above 160° deactivation of the "hot" vinylcyclopropane must be less efficient and isomerization competes. The cyclopentene produced by isomerization is also vibrationally excited as evidenced by the high yield of cyclopentadiene.

The product proportions at the higher temperatures bear a qualitative resemblance to those of Frey, who obtained products arising from a "hot" vinylcyclopropane produced by the addition of methylene to butadiene.³¹ In both cases the yields of the other products could be made to increase at the expense of vinylcyclopropane, although Frey produced the effect by decreasing the total pressure whereas in the present study it was done by increasing the thermolysis temperature. The effect of pressure on the products of thermolysis

FIGURE 12

ENERGY DIAGRAM FOR THERMOLYSIS OF XXVI AT 160°



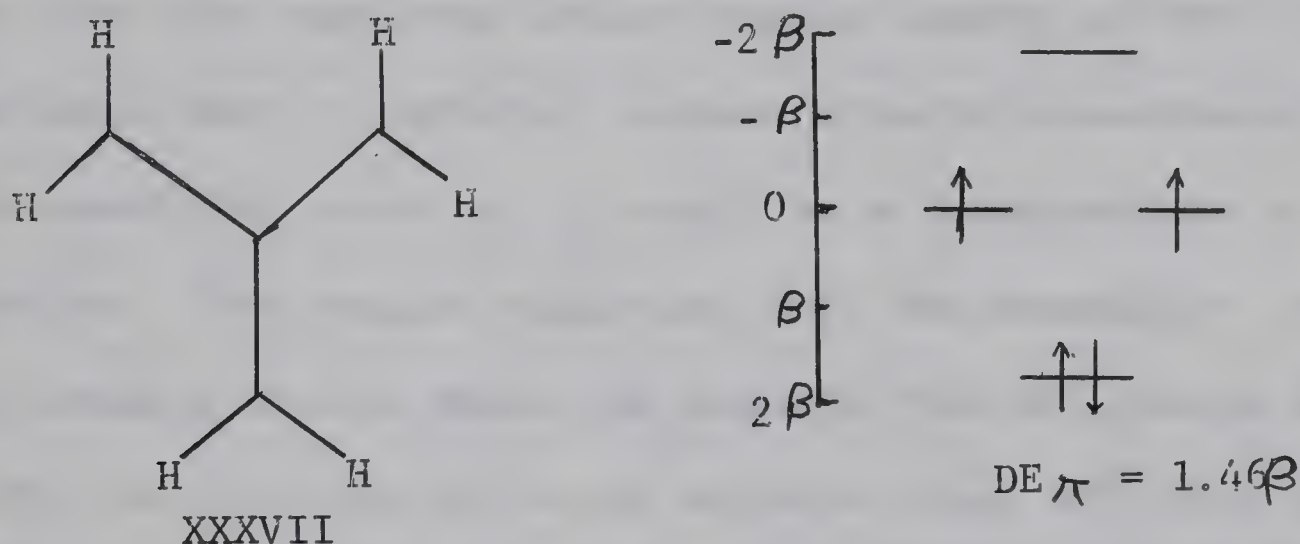
of XXVI is currently being studied by B. Strehlke. The results of Frey are complicated by the formation of insertion products as evidenced by the presence of isoprene, whose yield was pressure independent. Isoprene was not observed as a product of thermolysis of either XXVI or vinylcyclopropane.^{25,26}

CHAPTER III

TRIMETHYLENEMETHANE

(A) Introduction

The species trimethylenemethane (XXXVII) is of considerable theoretical interest because its central carbon atom is bonded by 3σ and 3π bonds to its neighbours making it possess the maximum possible bonding power for a carbon atom. Huckel molecular orbital (HMO) calculations place the total bond order⁵⁶



of the central carbon at 4.732. This figure is used as a basis for calculations of the free valence index (F_i) for any particular carbon atom (i), i.e.

$$F_i = 4.732 - \sum p_{ij}$$

where p_{ij} is the bond order between adjacent atoms i and j. The HMO calculations (Appendix I) also predict that XXXVII is a triplet in its ground state and that it possesses a high resonance energy ($DE_{\pi} = 1.46\beta$).

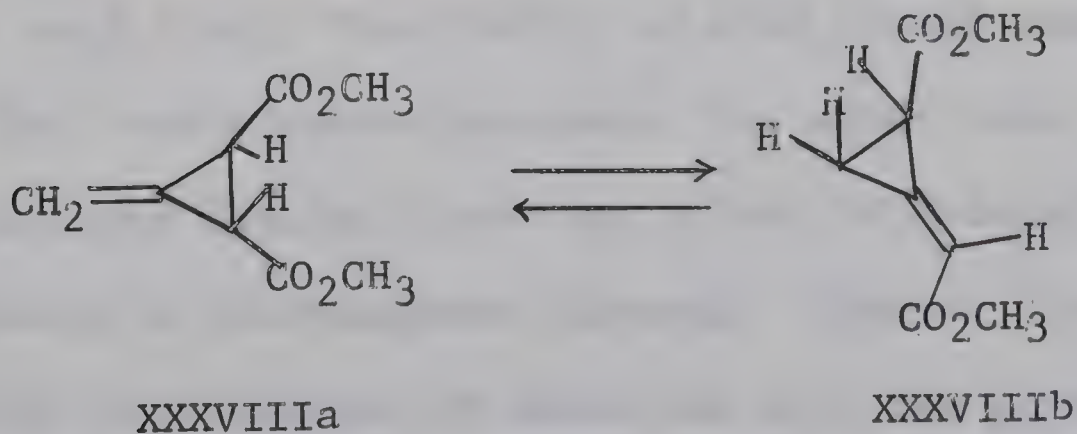
During the past few years there have been several reports of experiments where XXXVII may have been produced

experimentally. Chesick⁵⁷ observed that ethylidenecyclopropane and 1-methyl-2-methylenecyclopropane can be interconverted and he proposed a trimethylenemethane intermediate. The activation



energy for the process (40.6 kcal.) is 16 kcal. less than that predicted if there was complete steric inhibition of resonance in the transition state. Since the decrease is less than the predicted delocalization energy of XXVII he concluded that a completely planar trimethylenemethane is not the transition state but it could be an intermediate in the reaction. The results suggested that the transition state may actually be one where the plane of the HCR groups (R=H or CH₃) of the ring are at an angle of about 45° with the plane of the other carbon atoms.

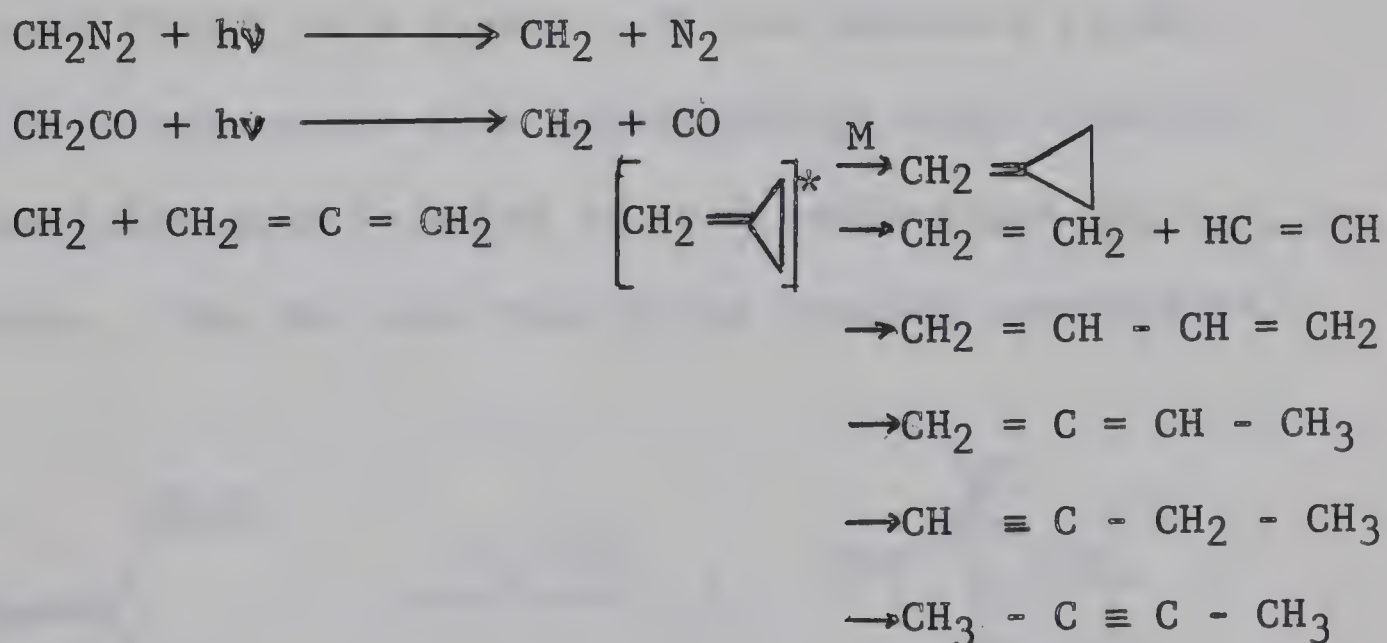
A similar rearrangement was observed by Ullman⁵⁸ upon thermolysis of Feist's ester XXXVIIIa. However, because of



the presence of electron-withdrawing groups a zwitterion intermediate might be involved rather than a substituted

trimethylenemethane species.

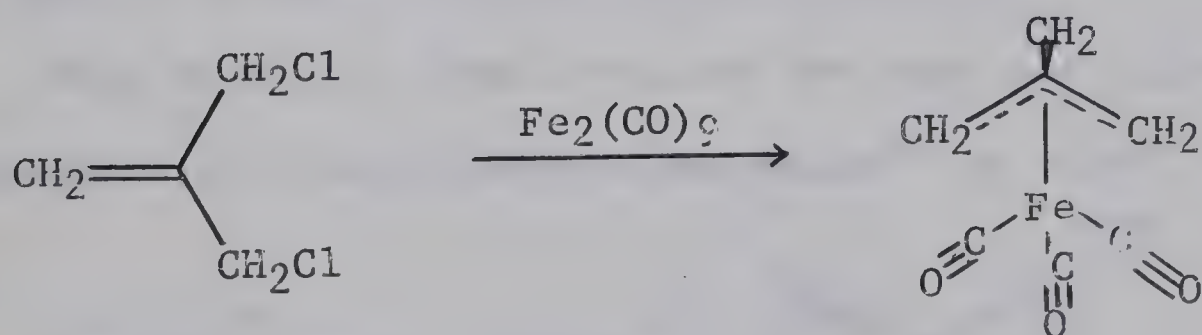
Frey⁵⁹ has studied the addition of methylene, produced by photolysis of diazomethane and ketene, to allene. The major product, methylenecyclopropane, is formed in a highly vibrationally excited state and unless stabilized by collision it undergoes various unimolecular transformations. The principal reaction of the excited species gives rise to a molecule of acetylene and a molecule of ethylene. Other reactions that were also observed were the isomerizations to 1,3-butadiene, 1,2-butadiene, dimethylacetylene and ethylacetylene.



It is very likely that XXXVII is also formed readily from the "hot" methylenecyclopropane, but since none of the carbon atoms were labeled there was no way to determine whether Chesick's rearrangement occurred. However, Doering⁶⁰ has observed incorporation of deuterium into the exo-methylene group on addition of CD₂ to allene in the gas phase, indicating that chemical rotation was occurring in the excited methylene-

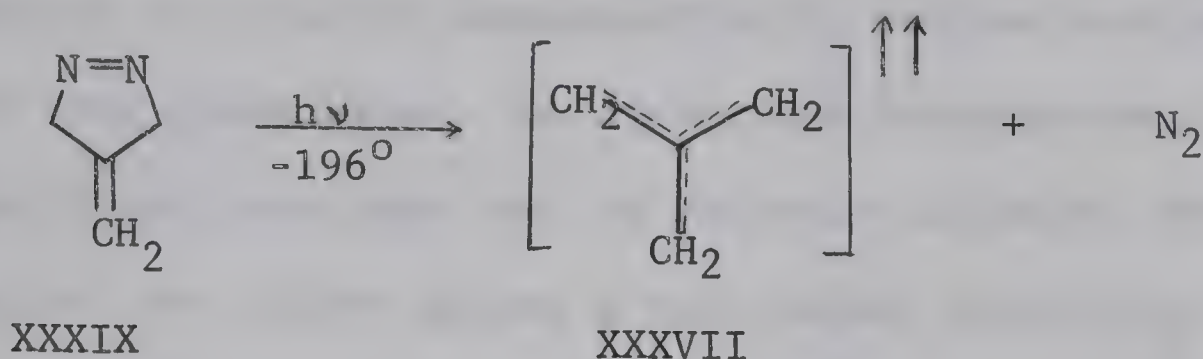
cyclopropane molecule. When he carried out the reaction in solution he found no deuterium in the exo-methylene group indicating that either the "hot" CD₂ is collisionally deactivated before addition or that the "hot" methylenecyclopropane formed is stabilized before it has a chance to isomerize.

In several instances it has been possible to prepare transition metal π -complexes containing as ligands organic molecules which are unstable in their free state. A good example is the iron tricarbonyl complex of cyclobutadiene prepared by Pettit, Emerson, and Watts.⁶¹ In a similar manner Emerson and coworkers⁶² have recently prepared a metal complex with XXXVII as a ligand. It was obtained in 30% yield by stirring excess iron enneacarbonyl with 3-chloro-2-chloromethylpropene in ether at room temperature for twelve hours. The nmr spectrum of the complex consists of



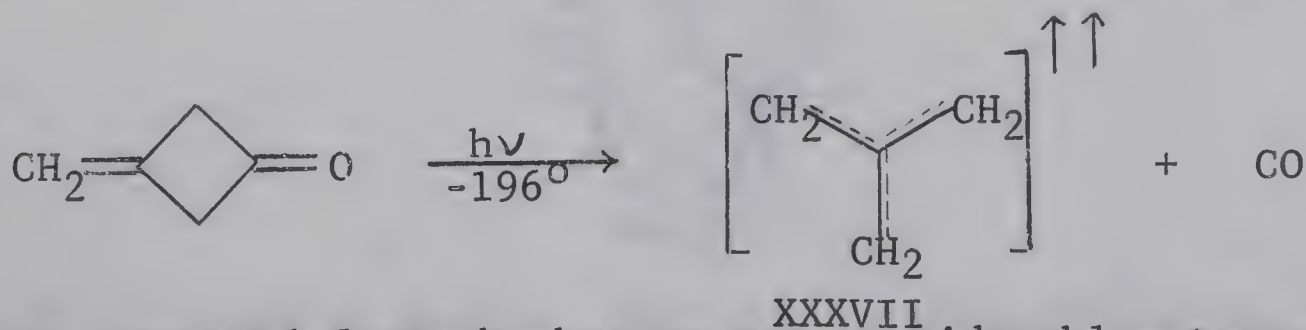
a lone singlet at τ 8.00, indicating the equivalency of all the hydrogens. This, as well as C¹³ nmr evidence, led Emerson to the conclusion that the complex is symmetrical and that the iron atom is situated directly beside the central carbon atom.

While the present investigation was in progress Dowd⁶³ obtained an electron spin resonance (esr) spectrum, at -196° , of an intermediate from the photolysis of 4-methylene-1-pyrazoline (XXXIX) with light of wavelength 315-335 mμ. Peaks were observed at 3024, 3152, 3428 and 3556 gauss.



The results suggested that the spectrum is due to the presence of a triplet state species which has a three-fold or higher axis of symmetry. The fact that the species gave the spectrum for a period of a month after irradiation when stored in liquid nitrogen supports the suggestion that the esr signal is due to a ground state triplet.

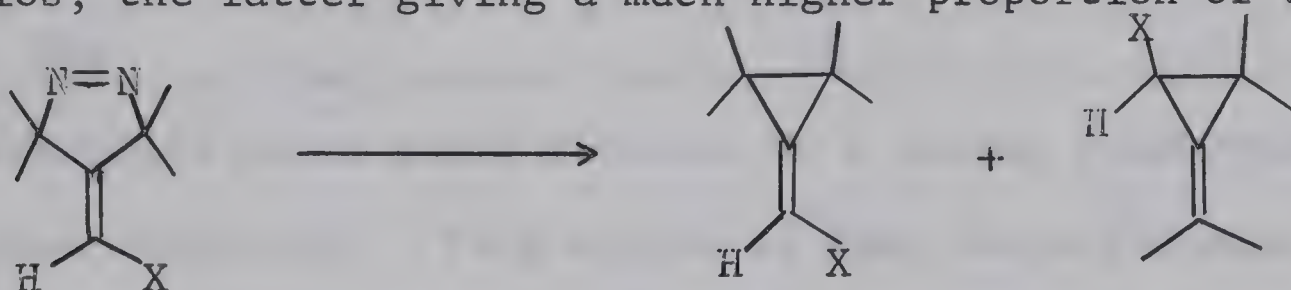
More recently, Dowd obtained the same esr signal by photolysis of 3-methylenecyclobutanone⁶⁴ at -196° . The



spectrum obtained from the ketone was considerably stronger and better resolved than any obtained from the pyrazoline. The strong spectrum from the ketone also allowed the observation of the $\Delta M = 2$ transition at 1590 gauss, which is further evidence that the spectrum is due to a triplet

species. The $\Delta M = 2$ transition is approximately 40 times less intense than the $\Delta M = 1$ transition and consequently could not be detected in the weaker pyrazoline spectrum.

The direct and photosensitized photolysis of the 3,3,5,5-tetramethyl-4-alkylidene-1-pyrazolines (XL) is the subject of a recent communication by Andrews and Day.⁶⁵ For both pyrazolines, the direct and benzophenone photosensitized reactions lead to entirely different product ratios, the latter giving a much higher proportion of the



XLa; X = Cl

XLb; X = OCOEt

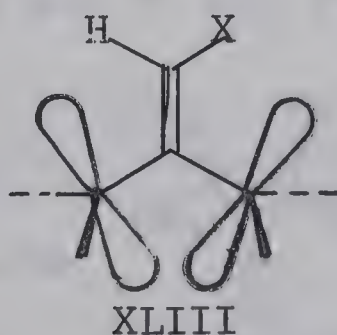
XLIIa; X = Cl

XLIIb; X = OCOEt

XLIIa; X = Cl

XLIIb; X = OCOEt

the "rearranged" isomer, XLII. They suggested that direct photolysis gives rise to a singlet intermediate such as XLIII, which is formed in a position where σ -bond formation



giving XLI readily occurs. For the photosensitized reaction, they suggested that a triplet pyrazoline is first formed, which upon loss of ground state nitrogen leads to a triplet intermediate. The longer lifetime of the triplet

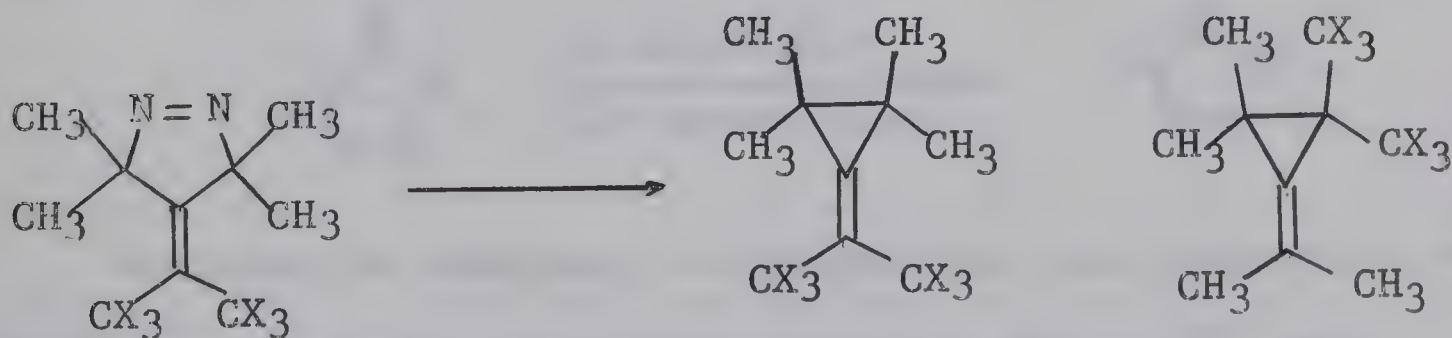
TABLE 13

PRODUCT PROPORTIONS FROM THE PHOTOLYSIS OF XL

	Relative Yields	
	XLI	XLII
Direct Photolysis		
XLa	77	23
XLb	64	36
Photosensitized $[(C_6H_5)_2CO]$		
XLa	25	75
XLb	18	82

intermediate would allow rotation to a planar trimethylene-methane derivative. They suggested that the preference of the triplet intermediate to form the cyclopropane XLII over XLI was due to electronic and possibly steric factors.

The thermolysis and photolysis of 4-isopropylidene-3,3,5,5-tetramethyl-1-pyrazoline (XLIII) has been studied by Mock.⁶⁶ Thermolysis of the deuterated compound (XLIIIb) at 500° gives both XLIV and XLV at the statistical ratio of 1:2.



XLIIIa; X = H
XLIIIb; X = D

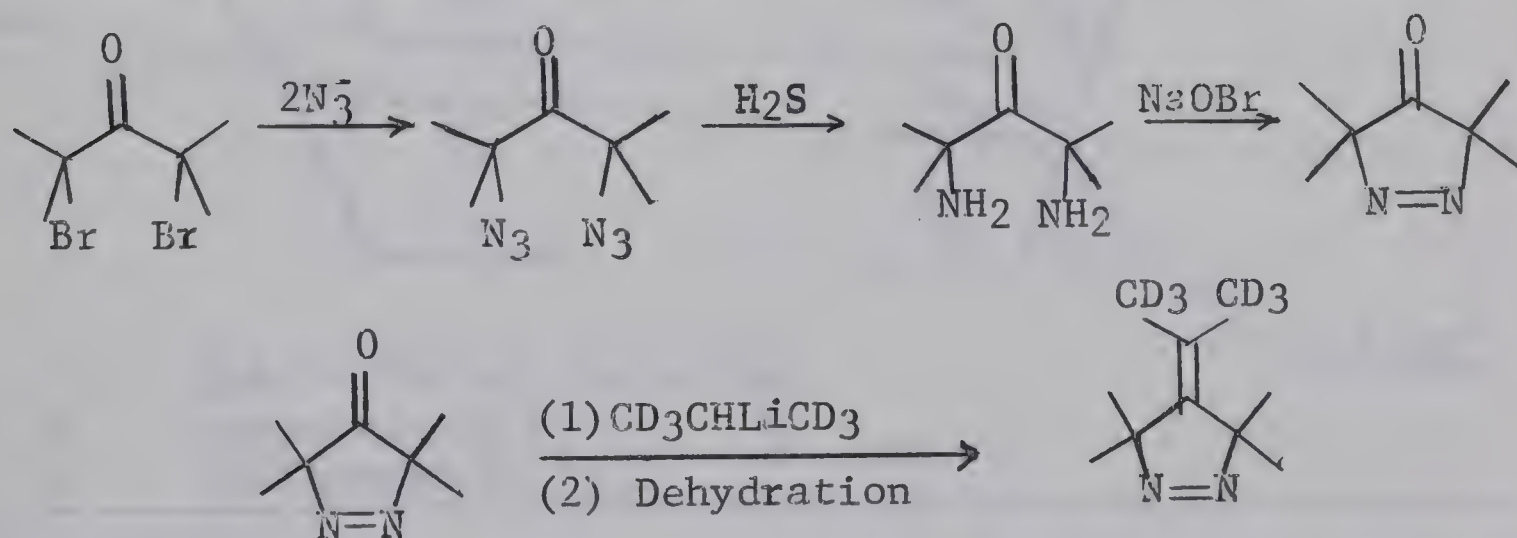
XLIVa; X = H
XLIVb; X = D

XLVa; X = H
XLVb; X = D

However, a control experiment showed that the products

rearrange under these thermolysis conditions, so it was impossible to determine whether XLIVb or XLVb is the major initial product of the thermolysis. Photolysis of XLIIIb gives only XLIVb in solution. It was also the only product of the gas phase photolysis when a pyrex filter was used, but 80% randomization occurs when the vapor was irradiated through quartz. Mock was unable to determine whether the observed retention is due to electronic effects or steric hindrance by the methyl groups preventing the formation of a planar intermediate.

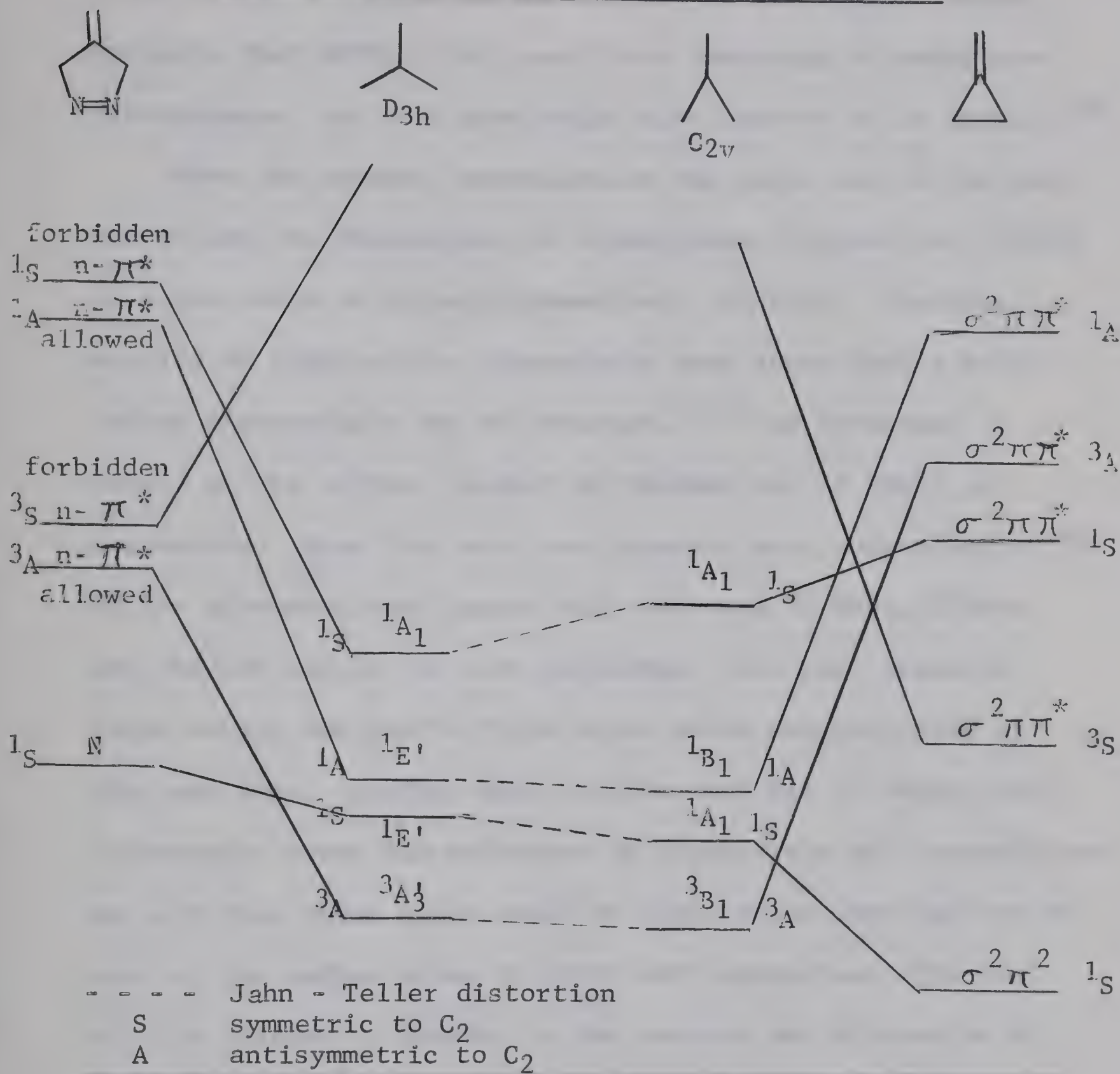
The method of synthesis that Mock used is noteworthy because his method is different than the three general methods for preparation of 1-pyrazolines mentioned at the beginning of Chapter II in this thesis.



Correlation diagrams for thermolysis and photolysis of XXXIX have recently been constructed by Borden.⁶⁷ The diagram for conrotatory reactions is shown in Figure 13. He predicts that thermolysis would lead to a singlet trimethylene-methane (XXXVII), which would readily close to methylenecyclo-

FIGURE 13

CORRELATION DIAGRAM FOR CONROTATORY REACTIONS



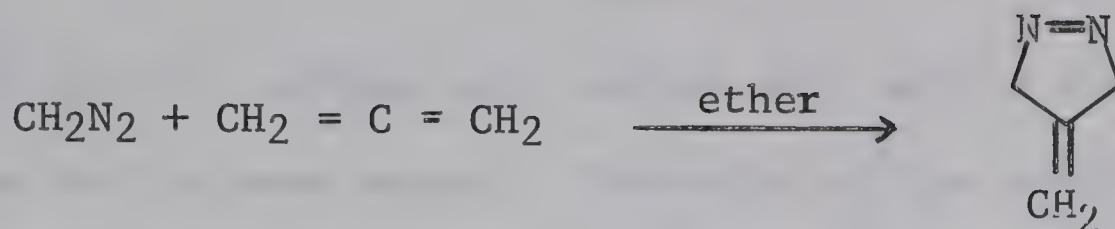
propane. From the orbital symmetry of the non-bonding MO he predicts that no deuterium scrambling would occur if one of the methylene groups is deuterated. This prediction has been shown to be invalid by experiments that are discussed later in this chapter. The diagrams support Dowd's suggestion that

the esr spectrum observed when XXXIX is photolyzed at -196° is due to XXXVII in its triplet ground state. Borden predicts that XXXVII ($^3A_3'$) would not rearrange to methylene-cyclopropane, but this prediction also appears to be invalid.⁶⁸

When the present investigation was begun one of the goals was to use the thermolysis of 4-methylene-1-pyrazoline (XXXIX) as a new route to trimethylenemethane (XXXVII). Previous studies on 1-pyrazoline thermolysis have shown that a hydrocarbon intermediate may be expected,^{1-5,8} so formation of XXXVII as the initial product of thermolysis of XXXIX is reasonable. When this work was reported as a communication,⁶⁹ of the aforementioned papers only the work of Frey, Ullman and Chesick had as yet been published. The rest appeared later except for Dowd's first paper which was published at the same time. Another goal of this work was to obtain more information about the mechanism of thermolysis of 1-pyrazolines. We felt that these goals could be achieved by labeling one or more of the carbon atoms of XXXIX with deuterium. The rest of this chapter is devoted to the results and discussion of these experiments.

(B) Syntheses

The synthesis of XXXIX by the addition of diazomethane to allene was reported by D'yakonov⁷⁰ in 1945. We first attempted the preparation by carrying out the reaction under the same conditions that were used for the addition of

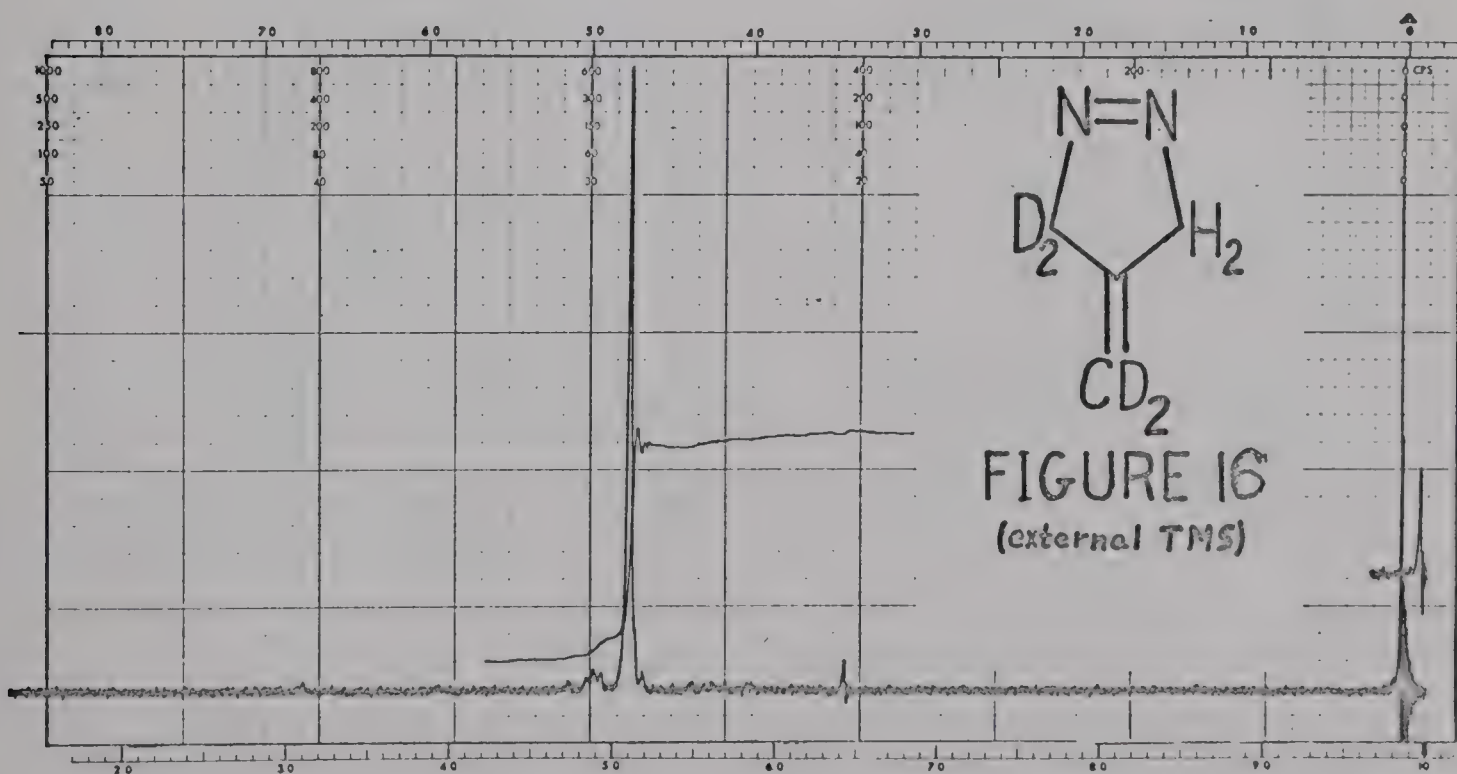
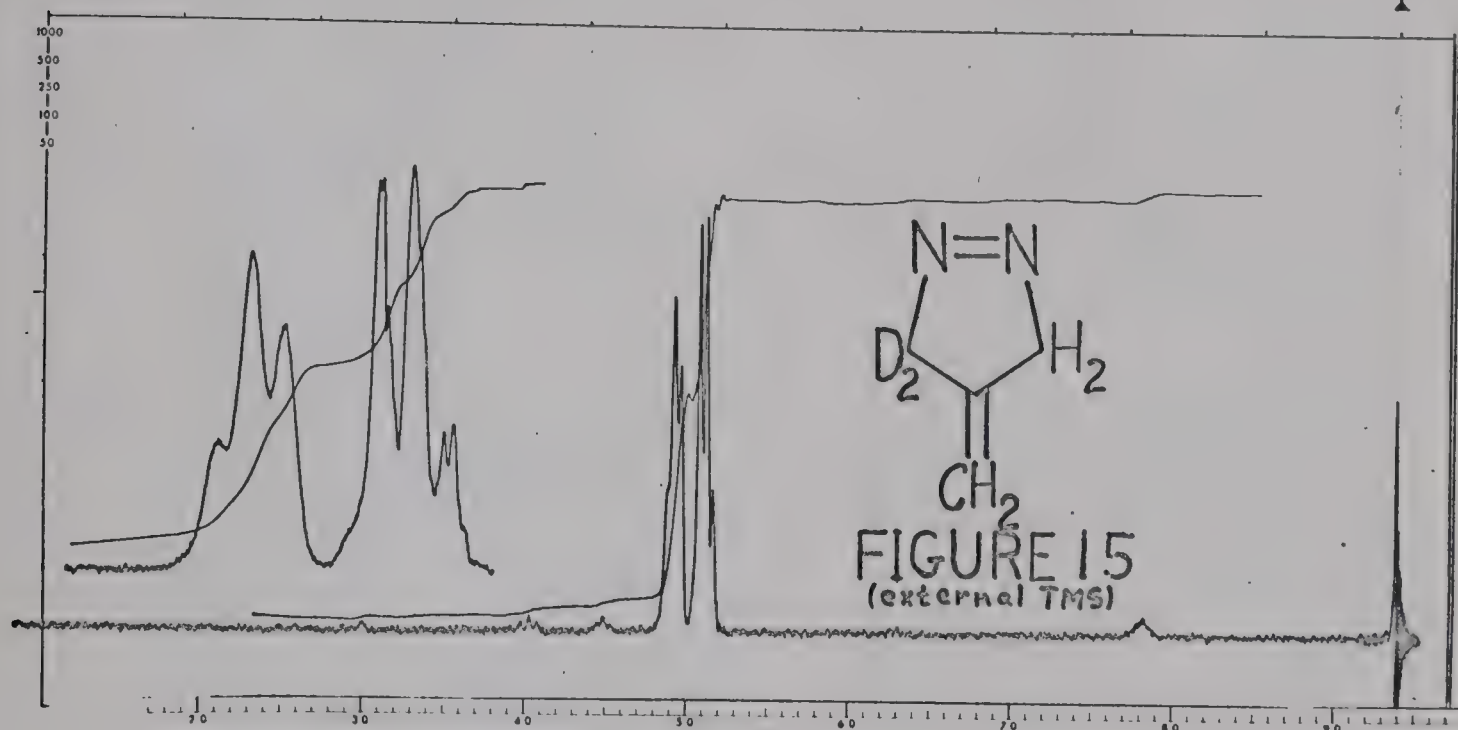
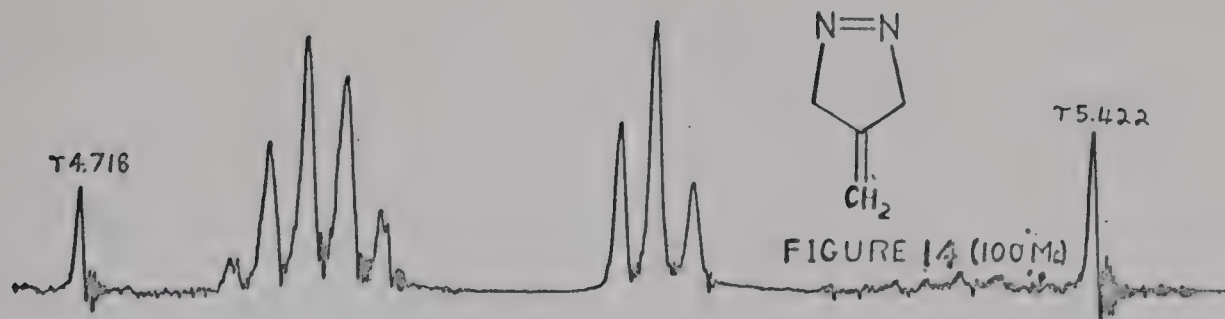


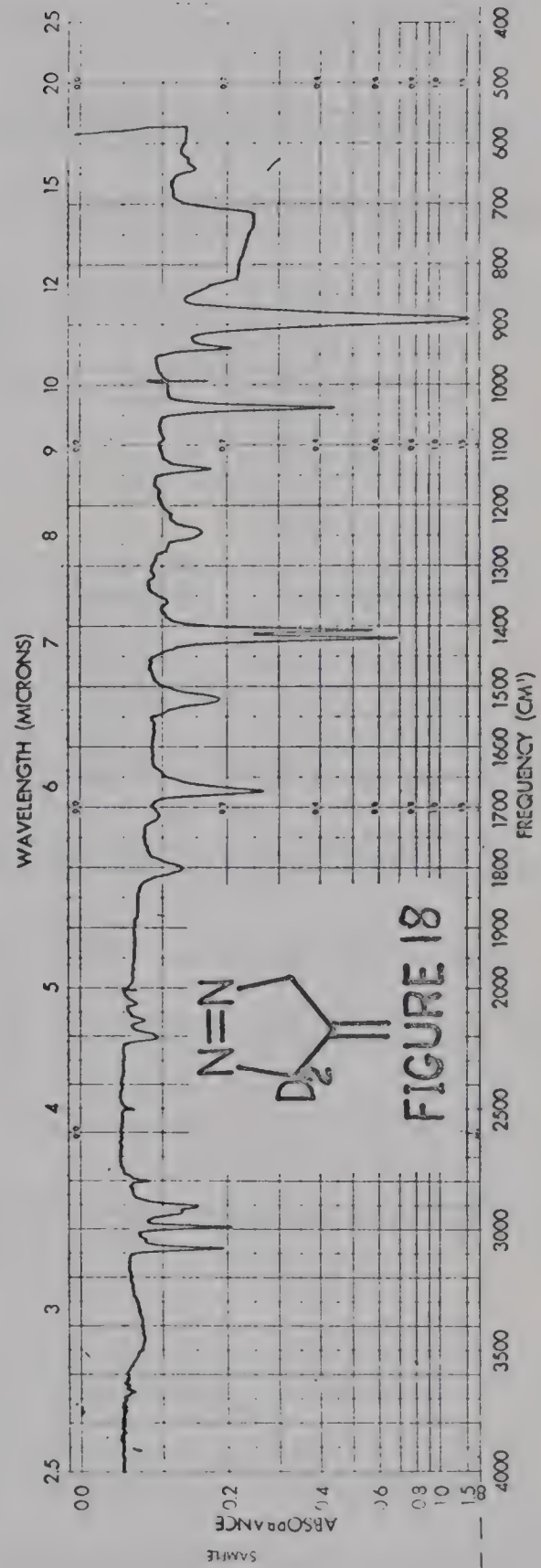
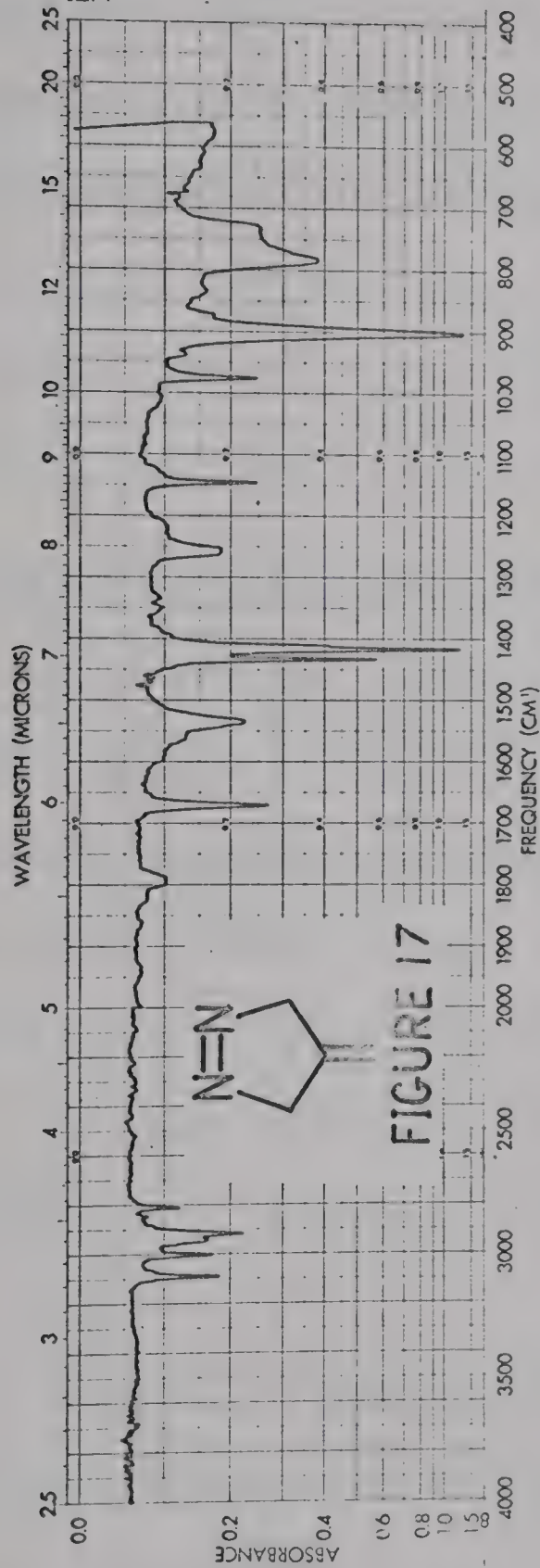
diazomethane to butadiene (i.e. a two-fold excess of allene in a 3% ethereal solution of diazomethane). However, the product was obtained in low yield and it contained a large amount of a tautomer that had an ultraviolet maximum at 290 mμ. The reaction was more successful when the ethereal diazomethane solution was concentrated by redistillation from 3% to approximately 12%, after which a three-fold excess of allene was added. After 15-20 hours at room temperature XXXIX was obtained in 70% yield.

Proof of the structure of XXXIX was obtained from the following data. Microanalysis is consistent with the formula $\text{C}_4\text{H}_6\text{N}_2$. In the mass spectrum the molecular ion has a mass of 82 also consistent with the formula $\text{C}_4\text{H}_6\text{N}_2$. The ultraviolet spectrum has a λ_{max} at 322 mμ ($\epsilon = 490$) in 95% ethanol, typical of 1-pyrazolines. The infrared spectrum (Figure 17) has no absorption above 3100 cm^{-1} indicating the absence of any nitrogen-hydrogen bonds. The bands at 1535 and 1670 cm^{-1} are consistent with the stretching modes of nitrogen-nitrogen and carbon-carbon double bonds. The nmr spectrum (Figure 14) consists of a quintet ($J = 2.6 \text{ c.p.s.}$) at $\tau 4.87$ and a triplet ($J = 2.6 \text{ c.p.s.}$) at $\tau 5.12$ with an intensity ratio of 1:2. The observed multiplicity is expected

if both vinylic protons are coupled with all of the allylic protons to the same extent. The value of the coupling constant (2.6 c.p.s.) is also typical for long range coupling between allylic and vinylic protons.

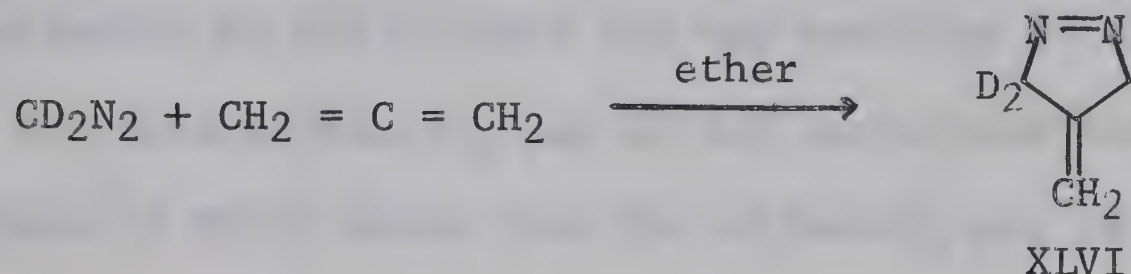
Small amounts of acid or base readily cause tautomerization of XXXIX to the 2-pyrazoline, 4-methylpyrazole and other unidentified high boiling products. After XXXIX was prepared two or three times in the same vessel, the walls of the vessel became coated with a basic material which caused tautomerization and a low yield of XXXIX. Therefore, later preparations were carried out in new pressure bottles. Separation of XXXIX from the tautomers was accomplished by fractional distillation of the product using a 30 cm. Vigreux column. The pure pyrazoline could be stored at -78° under a nitrogen atmosphere for periods of two to three weeks. If it was stored for longer periods redistillation was necessary before it could be used for kinetic studies. When XXXIX was allowed to remain at room temperature for only a few hours considerable tautomerization occurred. The nmr spectra which were observed daily on a sample of XXXIX kept at room temperature showed that a complex mixture of products gradually replaced XXXIX; two of these appeared to be 4-methylene-2-pyrazoline and 4-methyl-pyrazole. The latter was confirmed by isolation of the picrate (m.p. 141-142, lit.⁸³, m.p. 142) which





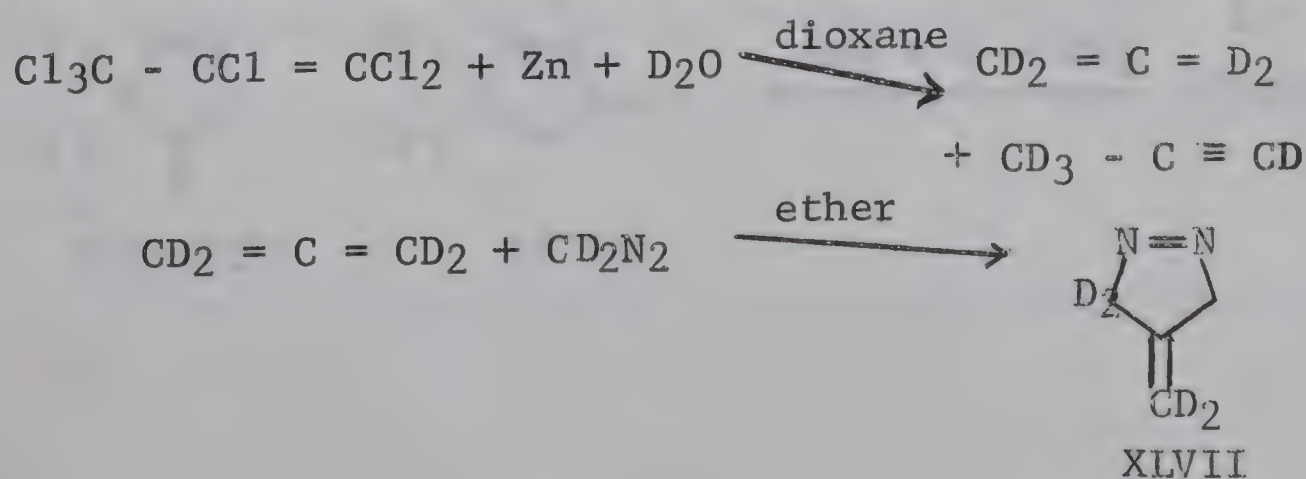
resulted from the addition of picric acid to a portion of the products. It is also necessary to store XXXIX under an inert atmosphere, because like other 1-pyrazolines, it turns yellow in the presence of air.

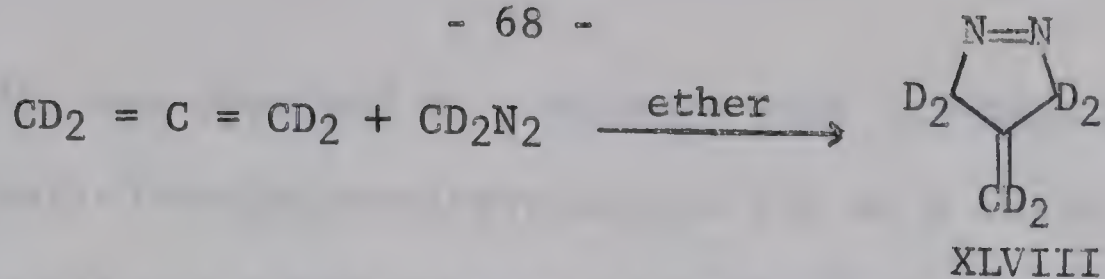
Preparation of 4-methylene-1-pyrazoline-3,3,d₂ (XLVI)
was accomplished by the addition of diazomethane-d₂ to allene.



The ultraviolet spectrum of XLVI was identical with that of XXXIX. Bands at 2200, 2140, 2070 and 1038 cm^{-1} in the infrared spectrum of XLVI (Figure 18) which are not present in the XXXIX spectrum are consistent with carbon-deuterium stretching and bending modes. Since the integrated intensities of the protons at τ 4.87 and τ 5.12 in the nmr spectrum of XLVI is 1:1, and since the resonance of the vinylic protons at τ 4.87 consists of a triplet, all of the deuterium must be in the 3-position.

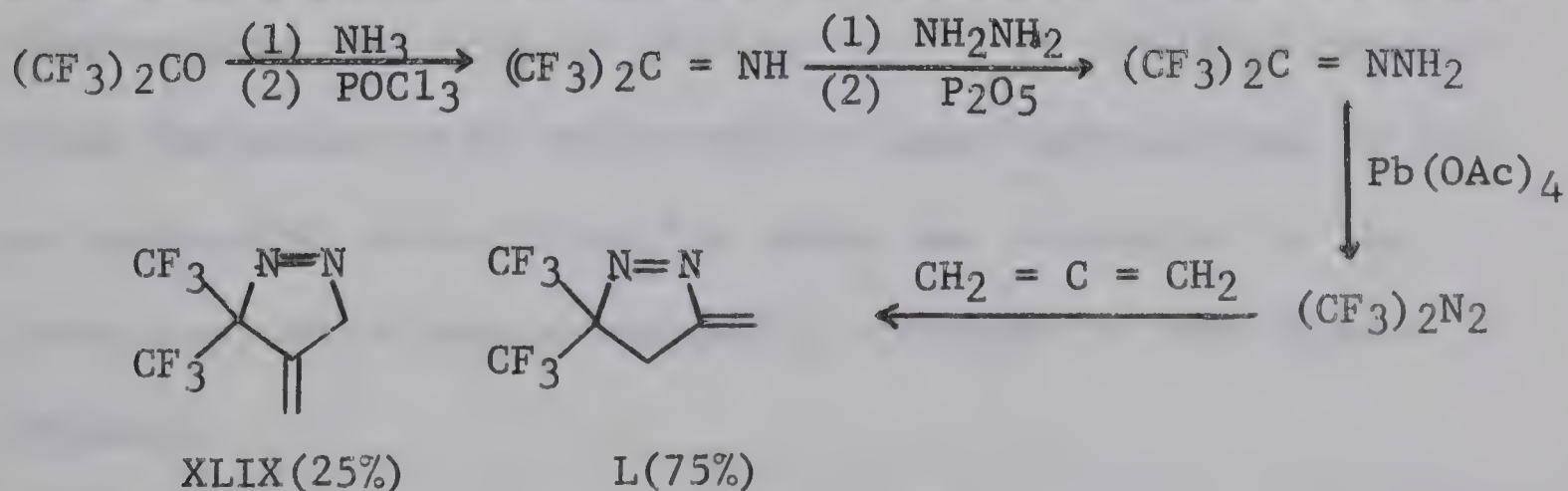
The addition of diazomethane to allene- $\underline{\text{d}}_4$ ⁷¹ gave 4-methylene-1-pyrazoline-3,3,6,6- $\underline{\text{d}}_4$ (XLVII). Similarly, addition of diazomethane- $\underline{\text{d}}_2$ to allene- $\underline{\text{d}}_4$ gave 4-methylene-1-





pyrazoline-3,3,5,5,6,6- d_6 (XLVIII). The nmr spectrum of XLVII consisted of a singlet at τ 5.12 and a very small peak at τ 4.87 indicating that the exomethylene group was greater than 95% deuterated. The extent of deuteration of XLVIII can be estimated at $95 \pm 3\%$ since the nmr spectrum of XLVI shows that the diazomethane- d_2 was 92-98% deuterated and the nmr spectrum of XLVII shows that the allene- d_4 was $>95\%$ deuterated. The allene- d_4 , together with some propyne- d_4 , was prepared by reacting zinc dust with hexachloropropene in a dioxane solution containing deuterium oxide. Most of the propyne- d_4 was removed by passing the products through an ammoniacal silver nitrate solution.

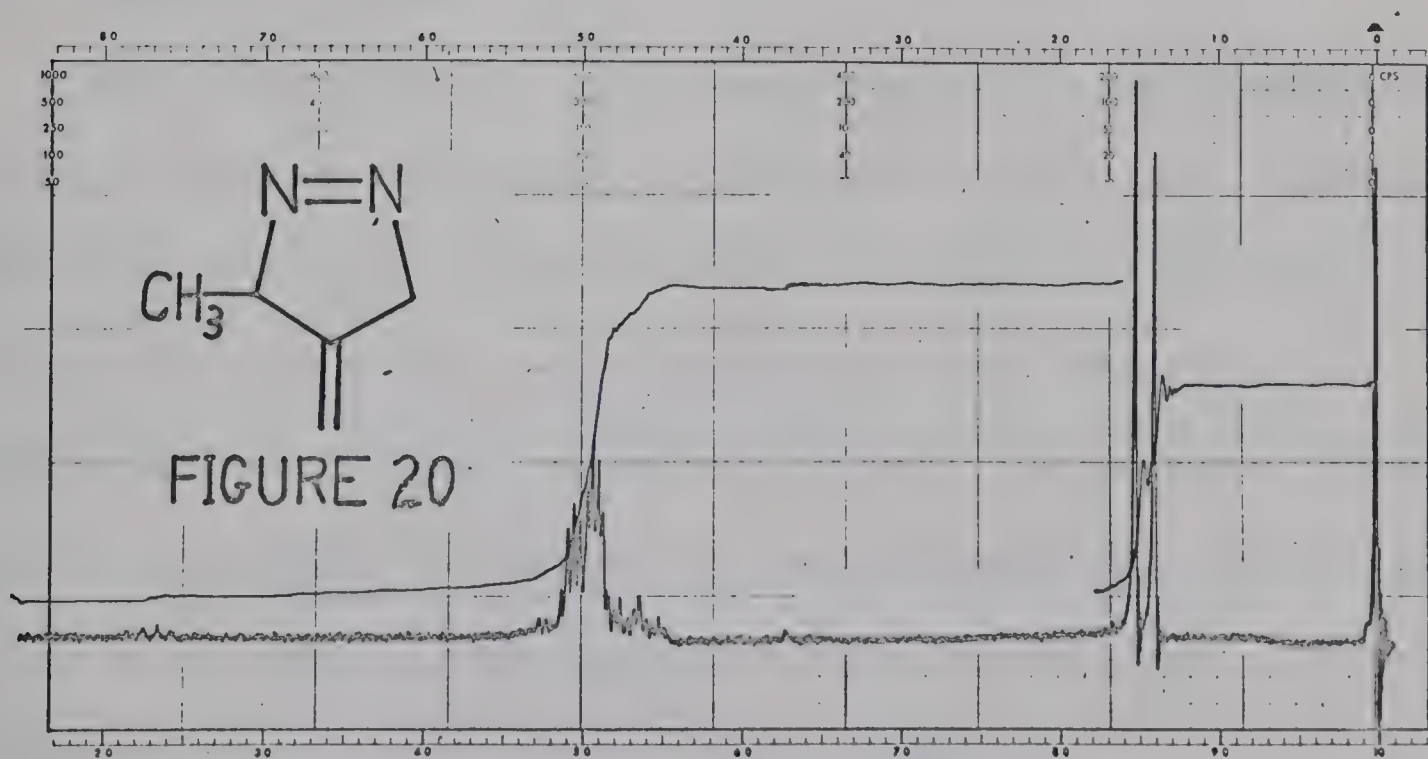
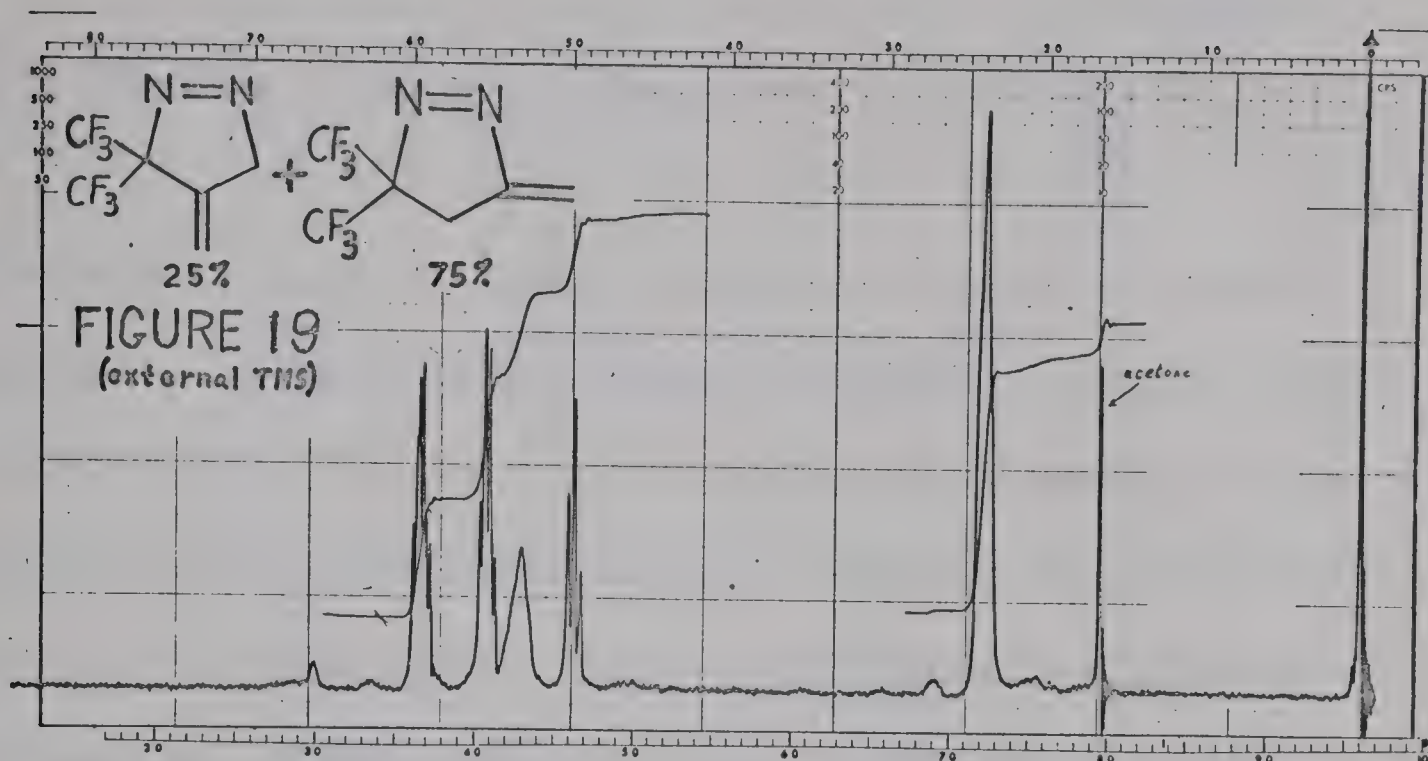
Preparation of 3,3-bis(trifluoromethyl)-4-methylene-1-pyrazoline (XLIX) involved the addition of bis(trifluoromethyl)-diazomethane to allene. The addition was found to be much slower than the addition of unsubstituted diazomethane to allene so a higher temperature was required. After 20 hours



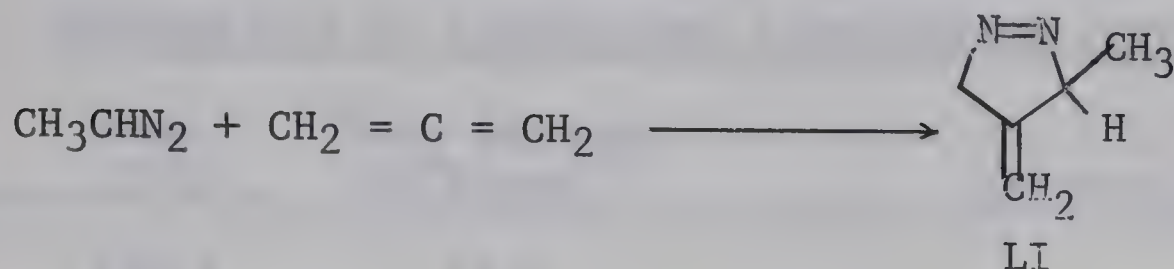
at 78° XLIX was obtained as a mixture with 5,5-bis(trifluoromethyl)-3-methylene-1-pyrazoline (L) at a ratio (XLIX/L) of 1:3 as shown by nmr. All attempts to separate the mixture failed. It was possible, however, to examine the thermolysis products at 155° because L is stable at that temperature. The nmr spectrum of XLIX (Figure 18) consists of a multiplet at τ 4.29 and a triplet ($J = 2.5$ c.p.s.) at τ 4.61 with an intensity ratio of 1:1. The peak at τ 4.29 is a multiplet because of long range coupling by fluorine. The F_{19} spectrum revealed that the coupling constant between the fluorines and the exo-methylene protons is 0.6 c.p.s.. Chemical shifts of τ 3.65, 4.07 and 7.25 at integrated intensity ratios of 1:1:2 are observed in the nmr spectrum of L. The low field protons show an AB pattern ($J_{AB} = 2.0$ c.p.s.) with each line also split into a triplet ($J = 2.5$ c.p.s.) due to long range coupling with the high field protons. Long range coupling with the fluorines ($J = 0.7$ c.p.s.) also causes the high field protons to exhibit a complex multiplet.

The method of preparation of bis(trifluoromethyl) diazomethane was that of Gale et al.⁷² It involved several steps beginning with conversion of hexafluoroacetone to the corresponding imine; then the imine was converted to the hydrazone, which was subsequently oxidized to the diazo-compound.

Addition of diazoethane to allene produced 3-methyl-4-



methylene-1-pyrazoline (LI). The MS-9 mass spectrum of LI showed that the molecular ion has an exact mass of 96.0691



consistent with the formula $\text{C}_5\text{H}_8\text{N}_2$ (calculated value = 96.0688). A multiplet between 4.8 and 5.4 and a doublet at 8.53 ($J = 7.0$ c.p.s.) at an intensity ratio of 5:3 constitute the nmr spectrum of LI (Figure 20). The ultraviolet spectrum is very similar to that of 4-methylene-1-pyrazoline (XXXIX) and has a λ_{max} at 326 m μ ($\epsilon = 290$, methanol).

(C) Kinetic Studies

The thermolysis of XXXIX was studied in the stainless steel reactor at temperatures between 165 and 188°. Table 14 shows the results of the kinetic runs together with the activation parameters calculated by an IBM 7040 computer from a method of least squares program. The computer also gave the standard deviation of the residuals from which the error in the activation parameters can be obtained. The probable error of the slope (P_m) is given by

$$P_m = P_y \sqrt{\frac{n}{n\sum x^2 - (\sum x)^2}}$$

where $P_y = 0.6745$ (standard deviation of residuals).

From the computer data

$$P_y = 0.6745 (0.0096327) = 0.00649$$

TABLE 14

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE
THERMOLYSIS OF 4-METHYLENE-1-PYRAZOLINE (XXXIX)

Run No.	Temp. (°C)	Rate Constant $10^4 k(\text{sec}^{-1})$	Activation Parameters
1	170.3	15.0	
2	174.25	21.3	
3	177.2	25.2	
4	176.5	25.0	$E_a = 32.6 \pm 0.3 \text{ kcal. mole}^{-1}$
5	179.75	32.8	$\log A = 13.24 \pm 0.15$
6	184.9	49.4	$\Delta S_{250}^\ddagger = -1.1 \pm 0.6 \text{ e.u.}$
7	187.9	61.7	
8	165.3	9.84	

$$P_m = 0.0649 \frac{8}{0.07529}$$

$$= 0.0668$$

The error in kcal mole^{-1} is $0.0668 \times 2.303 \times 1.987 = 0.30$,

so $E_a = 32.6 \pm 0.3$

The probable error of the intercept ($b = \log A$) is given

by

$$P_b = P_y \sqrt{\frac{\sum x^2}{n \sum x^2 - (\sum x)^2}}$$

$$= 0.00649 \sqrt{\frac{39.55}{0.07529}}$$

$$= 0.1485$$

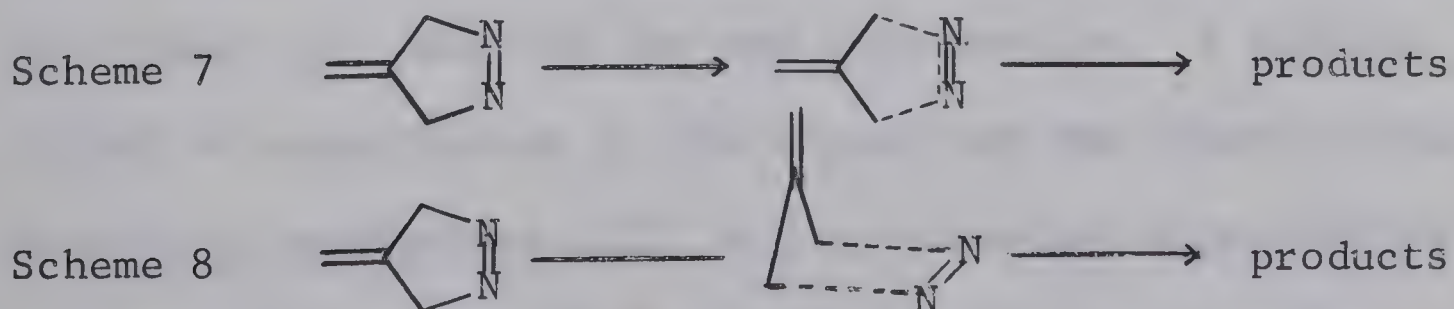
Therefore,

$$\log A = 13.24 \pm 0.15$$

$$\text{and } \Delta S_{250}^\ddagger = -1.1 \pm 0.6$$

Another source of error in the kinetic studies that required a great deal of attention was the presence of a small amount of acid or base in the reactor during a kinetic run. The sample of XXXIX had to be completely free of any of its basic tautomers or else tautomerization of the pyrazoline would compete with thermolysis. Also, the walls of the reactor had to be cleaned frequently because a film of basic material, which could not be pumped off, gradually formed on them during the kinetic runs.

The observed activation energy (32.6 ± 0.3 kcal mole⁻¹) represents a decrease of 9.6 kcal mole⁻¹ from that of 1-pyrazoline (I) (42.4 kcal mole⁻¹). The decrease is attributed to a contribution from the delocalization energy of trimethylenemethane (XXXVII) which is 1.46β from Huckel molecular orbital (HMO) calculations. A delocalization energy of 0.83β is obtained from the HMO calculations on the allyl system. If Benson's value for the allylic resonance energy (13 ± 1 kcal.)⁴⁷ is used then β would be about 16 kcal., which suggests that the delocalization energy of XXXVII is about 24 kcal. Scheme 7 shows a



planar transition state where no contribution from the resonance energy of XXXVII is expected because the new p orbitals that are forming would be orthogonal to the π -orbital of the double bond. In Scheme 8 the reaction proceeds through a bent transition state with the C_3C_5NN plane perpendicular to the $C_3C_4C_5$ plane, where the contribution from the resonance energy of XXXVII is expected to be close to 24 kcal.. Since the activation energies of thermolysis of I and XXXIX differ by only 9.6 kcal., a bent transition state is suggested but bond breaking cannot be extensive in the transition state.

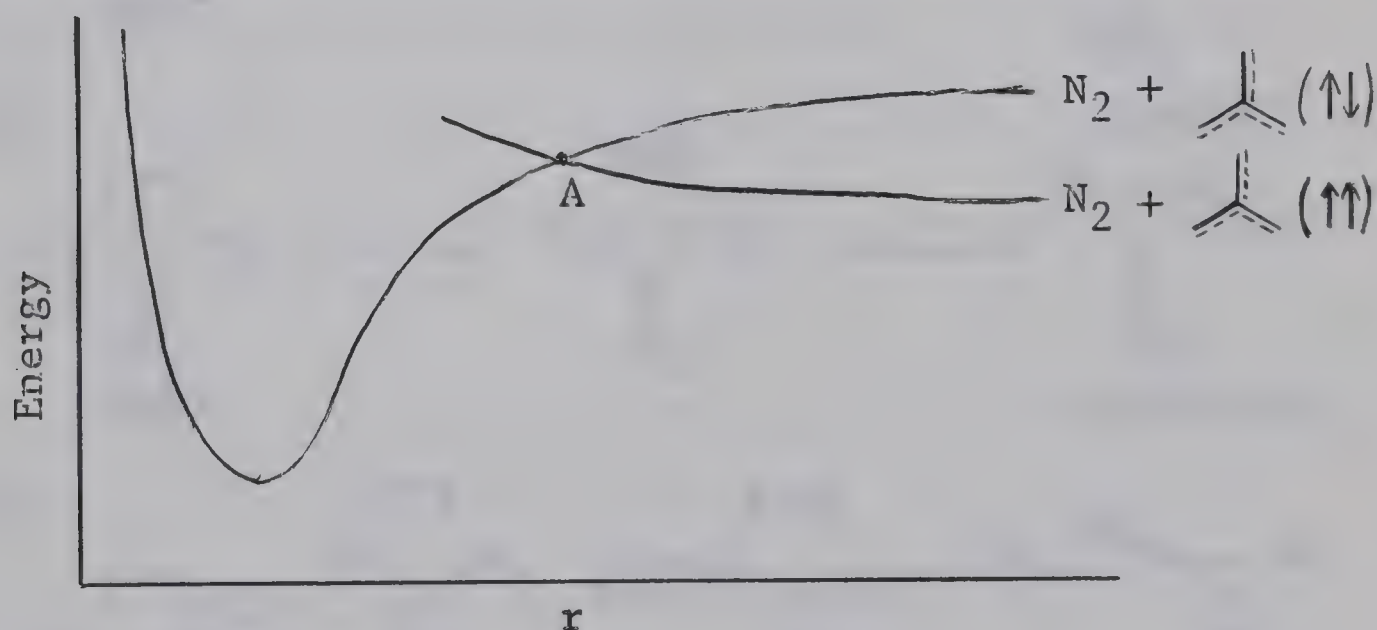
The difference, only 9.6 kcal, is possibly due to an unfavorable entropy for Scheme 8. As the angle between the C_3C_5NN and $C_3C_4C_5$ planes decreases, the repulsion between the filled π -orbitals of the carbon-carbon and nitrogen-nitrogen double bonds is expected to increase resulting in a lower free energy of activation. If Scheme 7 is involved E_a and ΔS_{250}^\ddagger would probably be somewhat similar to those for thermolysis of I, but if Scheme 8 is involved both parameters would likely be much lower. In fact, the ΔS_{250}^\ddagger for thermolysis of XXXIX was found to be -1.1 e.u., which is the lowest yet observed for any 1-pyrazoline. A similar effect of substitution in the 4-position was observed when 4-methyl-1-pyrazoline (III) and 4,4-dimethyl-1-pyrazoline (IV) were thermolyzed.^{1,5} Almost identical activation

energies are observed but the ΔS_{250}^\ddagger for IV is 7.9 ± 0.6 e.u. less than that for III. The decrease was attributed to steric compression in the transition state.

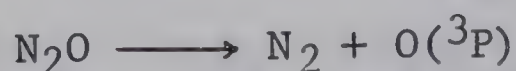
Another possible explanation of the low value of $\log A$ (13.24) is that the transmission coefficient (K) is less than unity. It was assumed to be unity in the calculation of ΔS_{250}^\ddagger . If intersystem crossing occurs during the thermolysis of XXXIX then the potential energy profile can be represented as in Figure 21. The transmission coefficient

FIGURE 21

POSSIBLE POTENTIAL-ENERGY PROFILE FOR THERMOLYSIS OF XXXIX



would be equal to the probability for transfer from the singlet to the triplet state at point A. This is the same treatment that was used by Stern and Eyring⁷³ for the reaction

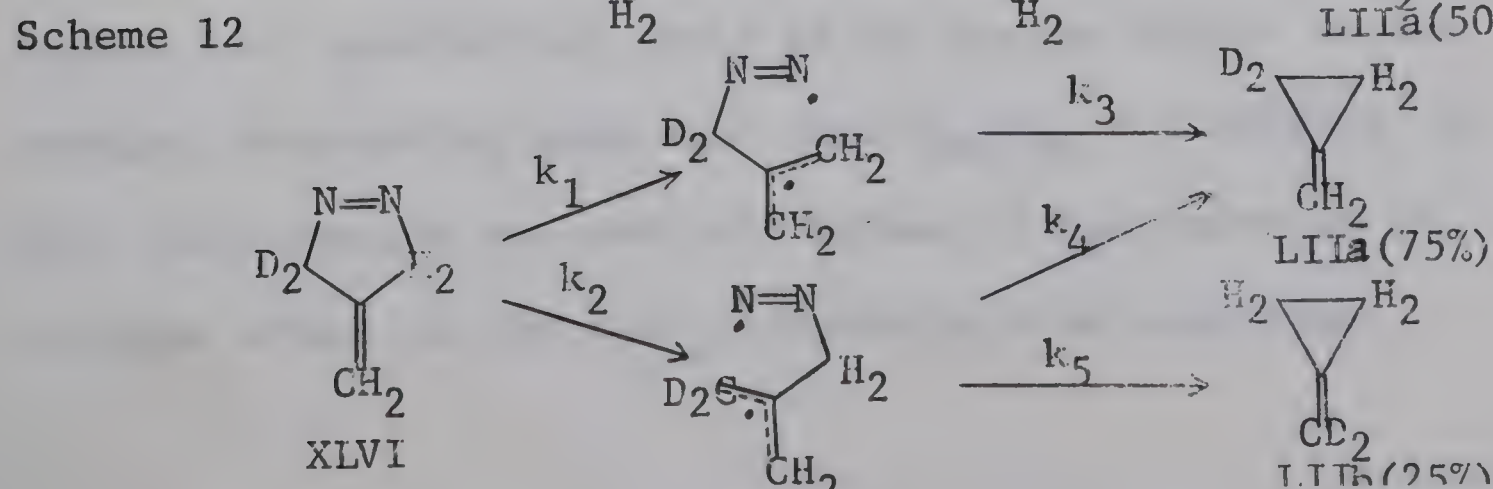
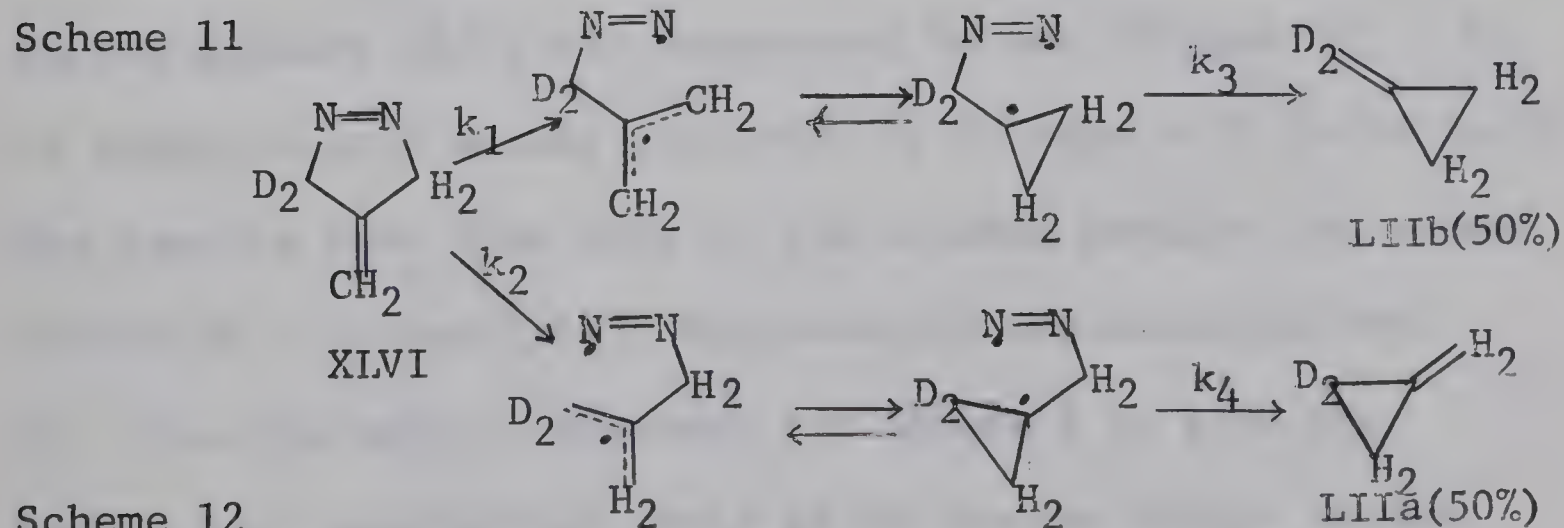
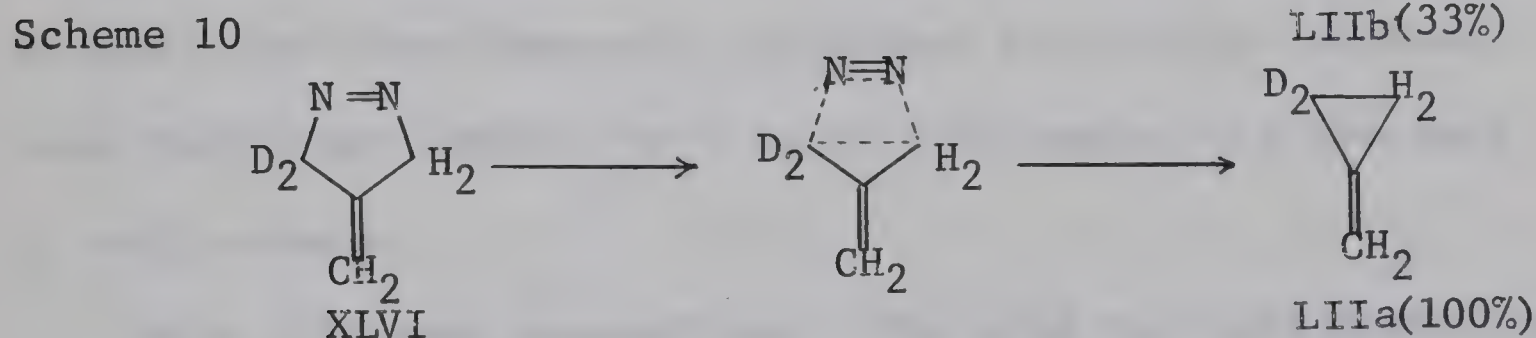
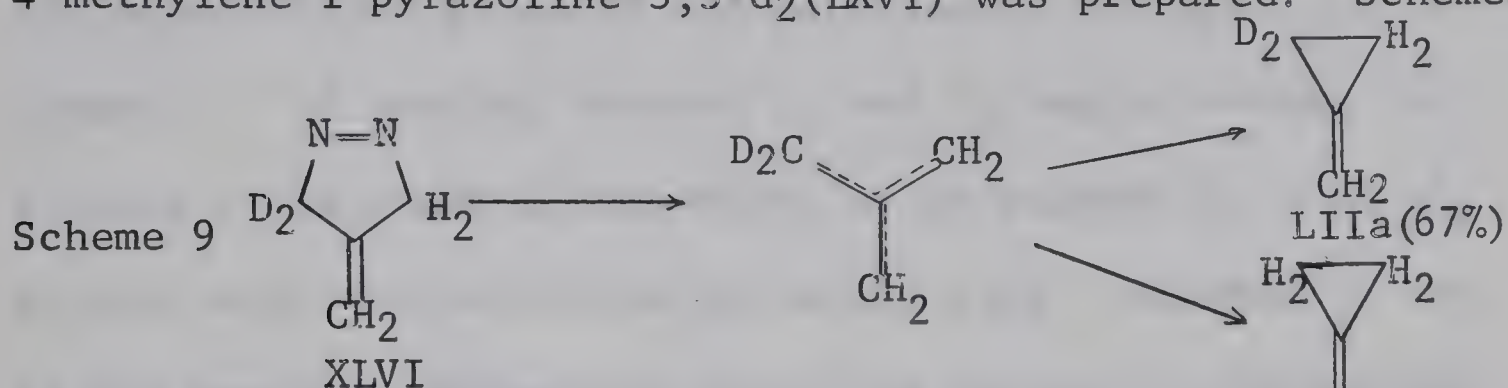


for which they estimated that $K = 10^{-4}$. For the thermolysis

of XXXIX, a small positive entropy of activation, which is normal for thermolysis of 1-pyrazolines,^{1,5} would be observed if $K = 10^{-1}$ to 10^{-2} .

(D) Product and Isotope Labeling Studies

An analysis of the thermolysis products of XXXIX showed that the only hydrocarbon product is methylenecyclopropane. In order to label one of the carbon atoms for mechanistic studies 4-methylene-1-pyrazoline-3,3-d₂ (XLVI) was prepared. Schemes



9-12 show four possible thermolysis mechanisms of XLVI and the position of the deuterium in the products as predicted by each mechanism assuming that there are no isotope effects. If trimethylenemethane (XXXVII) is an intermediate in the reaction, C₃, C₅ and C₆ would be expected to become equivalent in the intermediate, and if C₃ is deuterated then two-thirds of the deuterium would end up in the ring and one-third in the exomethylene group of the methylenecyclopropane as in Scheme 9. If bonding between C₃ and C₅ begins during the process of nitrogen elimination, as in Scheme 10, then all of the deuterium would end up in the ring. Schemes 11 and 12 are possible mechanisms where the carbon-nitrogen bonds do not break simultaneously. Nitrogen containing intermediates that react rapidly in a particular manner are involved in both schemes.

When XLVI was thermolyzed, the ring to vinyl proton ratio in the product (R/V) was determined by nmr (Figure 22). It is compared with values predicted by Schemes 9-12 in Table 15. The results show that none of the schemes predict the actual yields of LIIa and LIIb. Two possible explanations are:

- (i) the thermolysis proceeds via Scheme 9 to give the symmetrical species but there is an isotope effect in the product determining step such that $k_{HH}/k_{HD} = 1.37 \pm 0.05$, or
- (ii) the reaction proceeds via Scheme 11 but there is an isotope effect in the rate determining step such that

TABLE 15

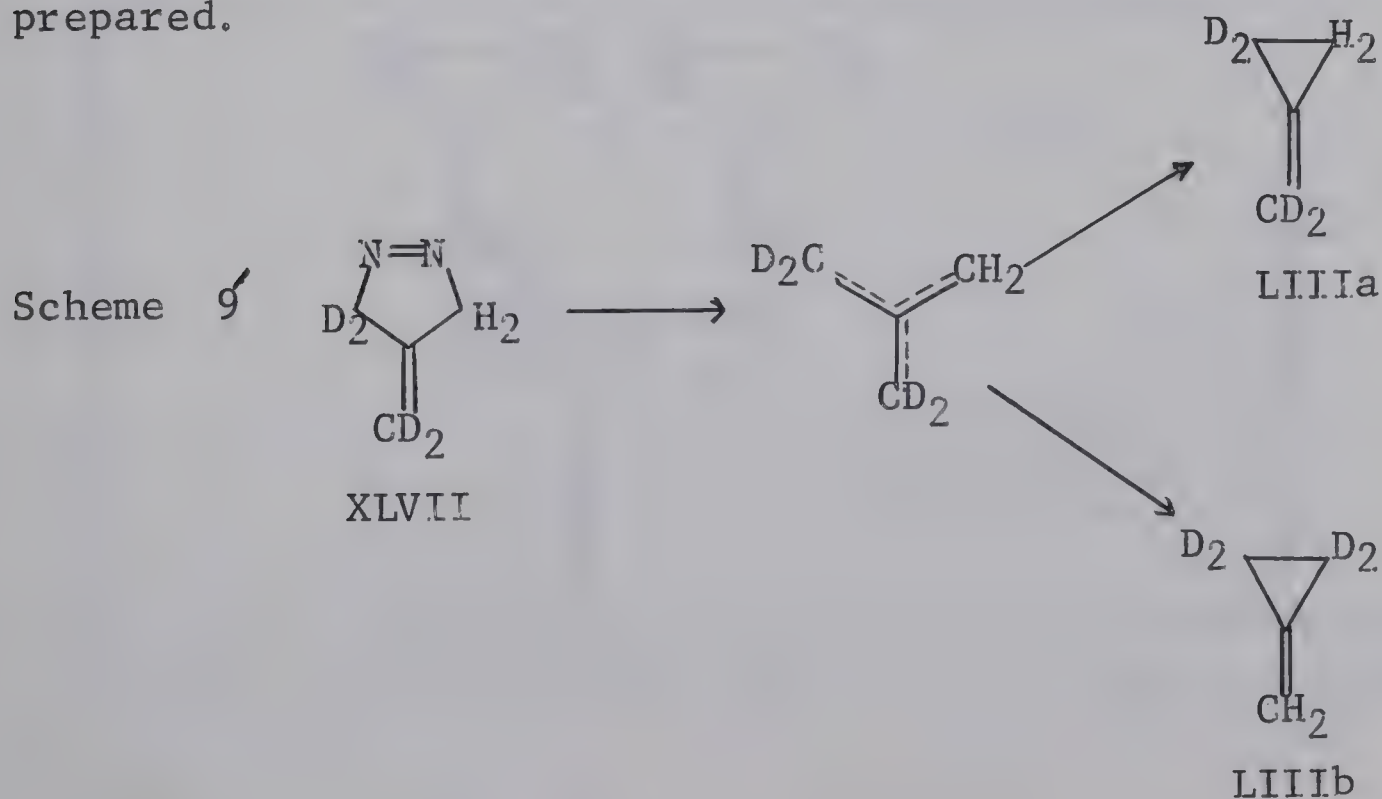
PREDICTED AND OBSERVED THERMOLYSIS PRODUCTS OF XLVI

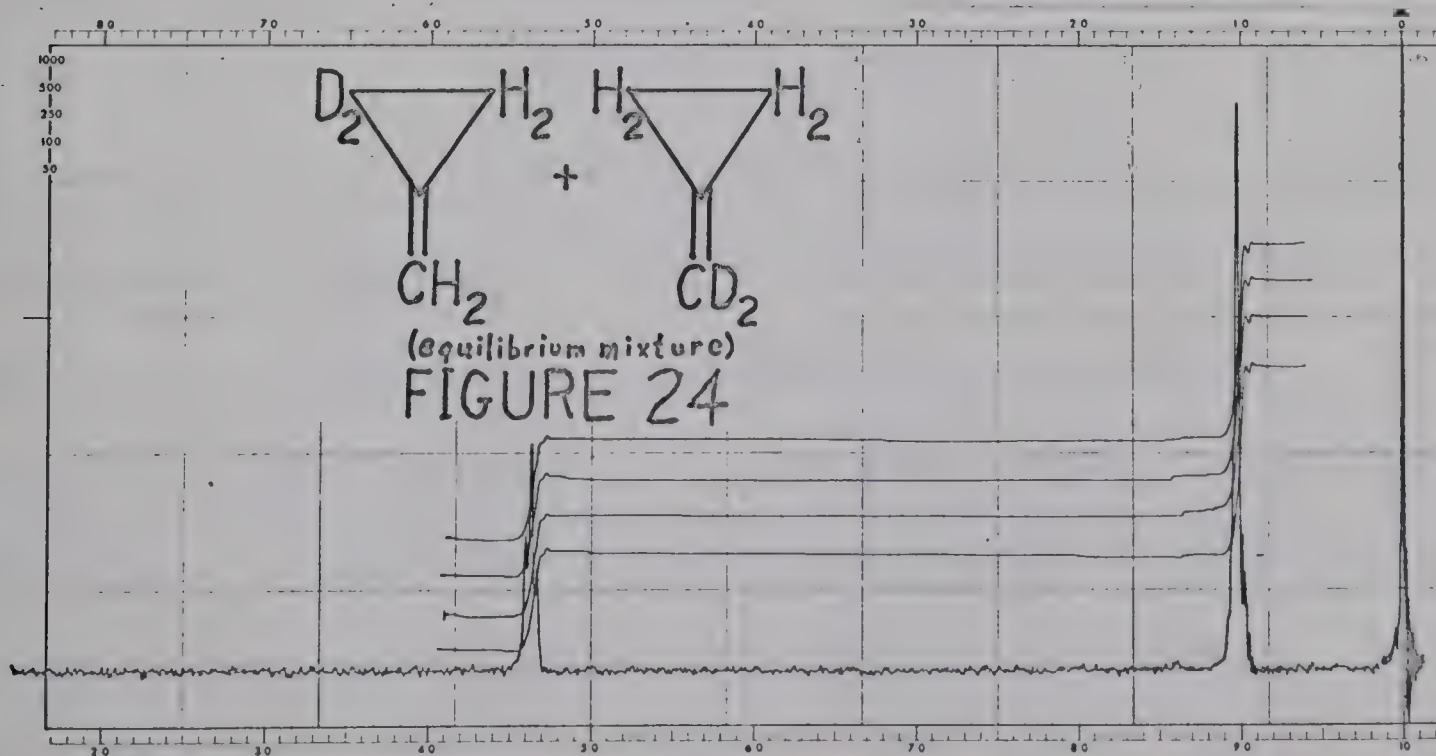
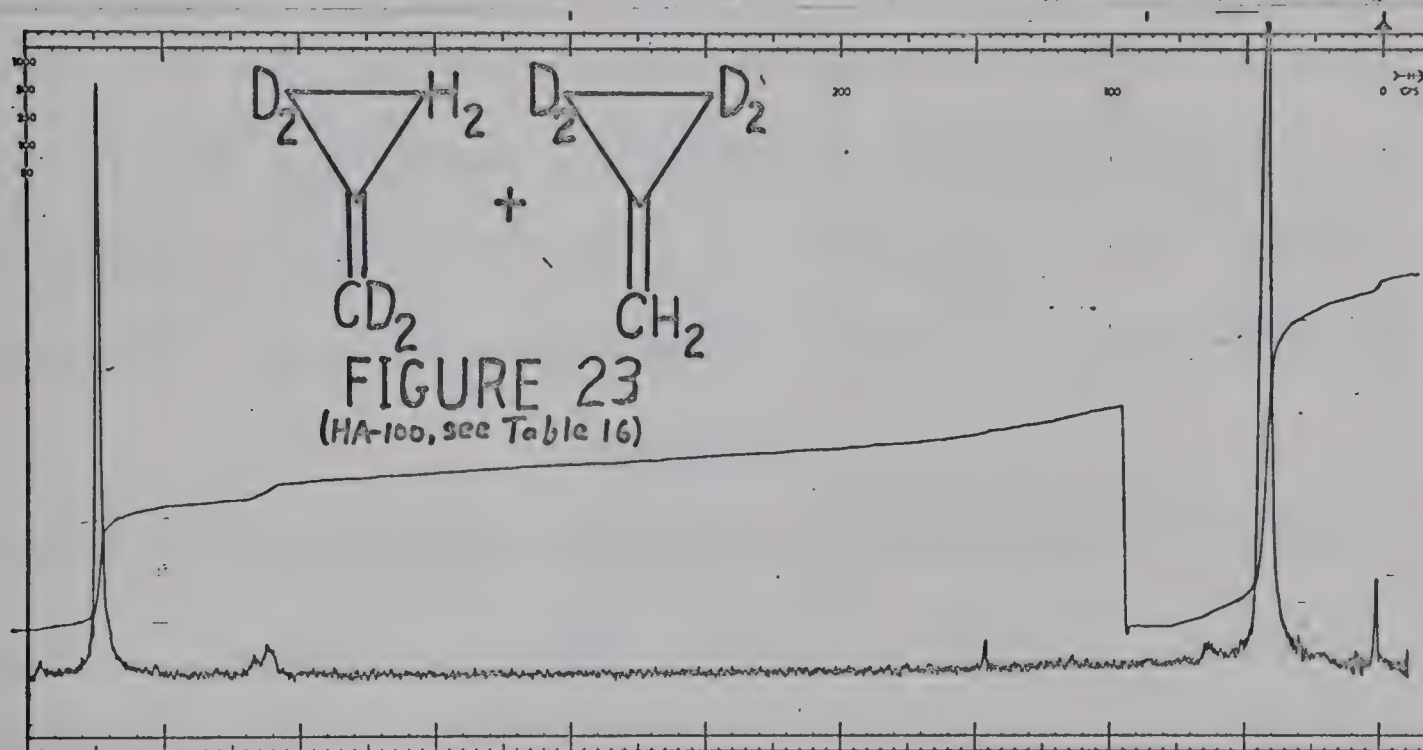
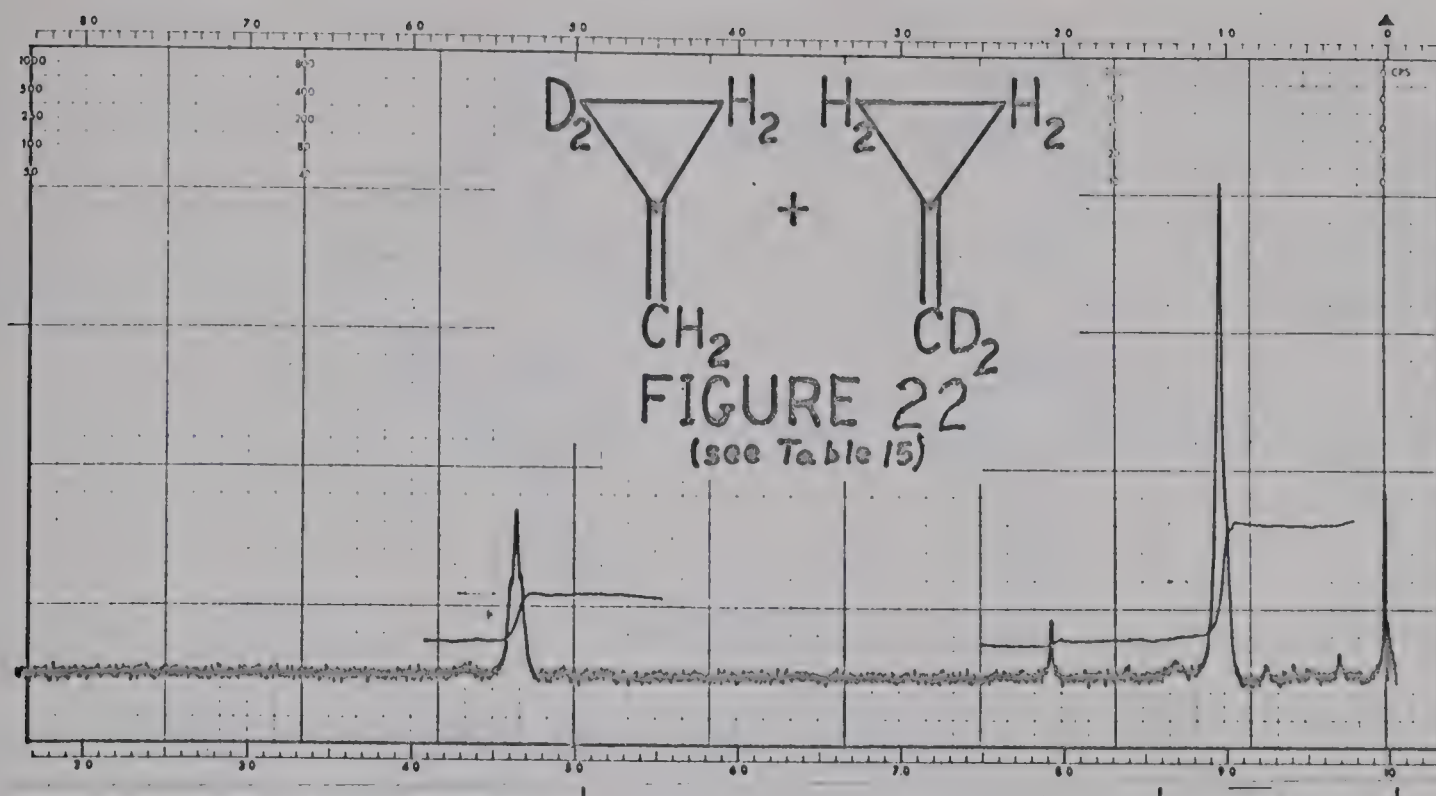
	R/V ^a	LIIa(%)	LIIb(%)
Scheme 9	2.0	67	33
Scheme 10	1.0	100	0
Scheme 11	3.0	50	50
Scheme 12	1.6	75	25
Observed	2.37 [±] 0.04	59.3 [±] 0.7	40.7 [±] 0.7

(a) R/V = ratio of integrated intensities of ring to vinyl protons in the nmr spectrum of LIIa + LIIb.

$k_2/k_1 = 1.46 \pm 0.06$. The experimental results conclusively rule out Scheme 10. Scheme 12 can also be ruled out because it requires a secondary isotope effect such that $k_1/k_2 = 0.25$ or $k_5/k_4 = 4.0$, which is very improbable.

In order to determine which of the preceding explanations is correct, 4-methylene-1-pyrazoline-3,3,6,6- d_4 (XLVII) was prepared.





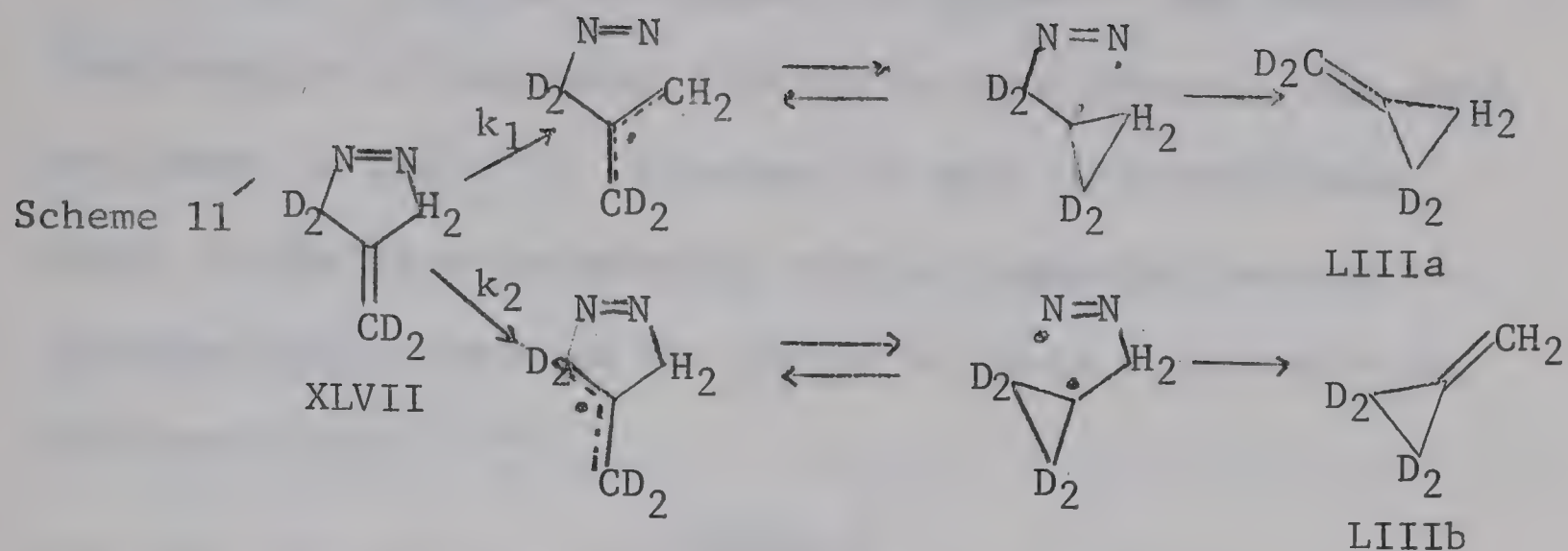


Table 16 shows the yields of LIIIIa and LIIIIb predicted by Scheme 9' when the assumption that $k_{HH}/k_{HD} = k_{HD}/k_{DD} = 1.37$ is made, as well as the values predicted by Scheme 11' using $k_2/k_1 = 1.46$. The observed yields of the products of thermolysis of XLVII at 175° , as determined by nmr (Figure 23) (Table 16), are within experimental error of those predicted

TABLE 16

PREDICTED AND OBSERVED PRODUCTS OF THERMOLYSIS OF XLVII

	R/V	LIIIIa	LIIIIb
Scheme 9'	2.74 ± 0.10	73.2 ± 2	26.8 ± 2
Scheme 11'	0.68 ± 0.06	40.7 ± 2	59.3 ± 2
Observed	2.82 ± 1.0	73.8 ± 0.8	26.2 ± 0.8

by Scheme 9'. Therefore, trimethylenemethane is an intermediate in the thermolysis of 4-methylene-1-pyrazoline.

Scheme 9' is the mechanism that one would expect by analogy with Mishra's results^{1,2,5} on the thermolysis of 4-deuterio-4-methyl-1-pyrazoline, which are discussed in Chapter I of this thesis.

Further evidence in support of Scheme 9 was obtained from studies of secondary kinetic isotope effects. The data are shown in Table 17. Cleavage of both carbon-nitrogen bonds in the rate-determining step is suggested because the isotope effect observed for XLVIII is about double that for XLVI and XLVII.¹¹⁻¹⁴

TABLE 17
SECONDARY KINETIC ISOTOPE EFFECTS IN THE THERMOLYSIS
OF DEUTERATED 4-METHYLENE-1-PYRAZOLINES

Temp.	Compound	Observed $10^4 k(\text{sec}^{-1})$	Corrected ^a $10^4 k(\text{sec}^{-1})$
167.75	XLVI	9.9 ± 0.2	9.7 ± 0.2
167.75	XXXIX	12.2 ± 0.1^b	12.2 ± 0.1^b
169.0	XLVII	10.6 ± 0.2	10.5 ± 0.2
169.0	XXXIX	13.6 ± 0.1^b	13.6 ± 0.1^b
172.9	XLVIII	11.9 ± 0.2	11.7 ± 0.2
172.9	XXXIX	18.7 ± 0.1^b	18.7 ± 0.1^b

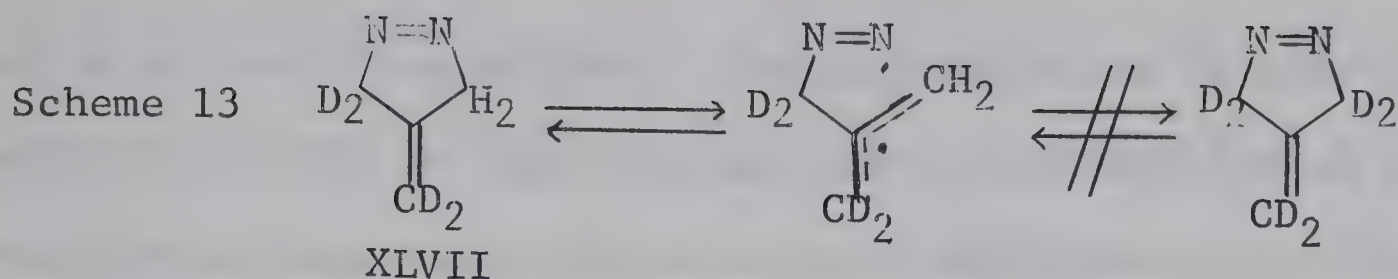
$$k_H/k_D = 1.26 \pm 0.03$$

$$k_H/k_D = 1.30 \pm 0.03$$

$$k_H/k_D = 1.60 \pm 0.03$$

- (a) Corrected for incomplete deuteration $[k_D = (k_{\text{obs}} - k_H f_H) f_D]$, where f_D is the fraction deuterated.
- (b) Calculated from the Arrhenius equation ($\log k = 13.24 - 32,600/2.303RT$)

If the thermolysis of XLVII proceeded via Scheme 11' then one might expect some hydrogen to be incorporated into the exo-methylene group via Scheme 13. When the thermolysis was stopped after one half-life, a nmr spectrum on the remaining pyrazoline was identical to that of the initial XLVII. The



results rule out Scheme 13 and provide further evidence against Scheme 11'.

The question of whether or not the intermediate involved in the thermolysis of XXXIX is triplet trimethylenemethane cannot be answered from the foregoing data. The data show that a symmetrical species where all the methylene groups become equivalent is involved, but it may be a singlet as suggested by Borden.⁷¹ From spin conservation the intermediate is expected to be formed in the singlet state, from which the rate of closure to methylenecyclopropane may be greater than the rate of intersystem crossing to the triplet state. Attempts to trap the intermediate by carrying out the thermolysis of XXXIX in cyclohexene and diethylfumarate solutions failed, which indicates that the lifetime of the intermediate is relatively short. A triplet trimethylenemethane might have a long enough lifetime to allow it to undergo bimolecular reactions.

Borden predicts, from orbital symmetry considerations, that XLVI may give only LIIa and XLVII would give only LIIIa. The possibility that a vibrationally excited LIIa is the initial product, which subsequently rearranges to give the thermodynamic equilibrium mixture of LIIa and LIIf, was ruled

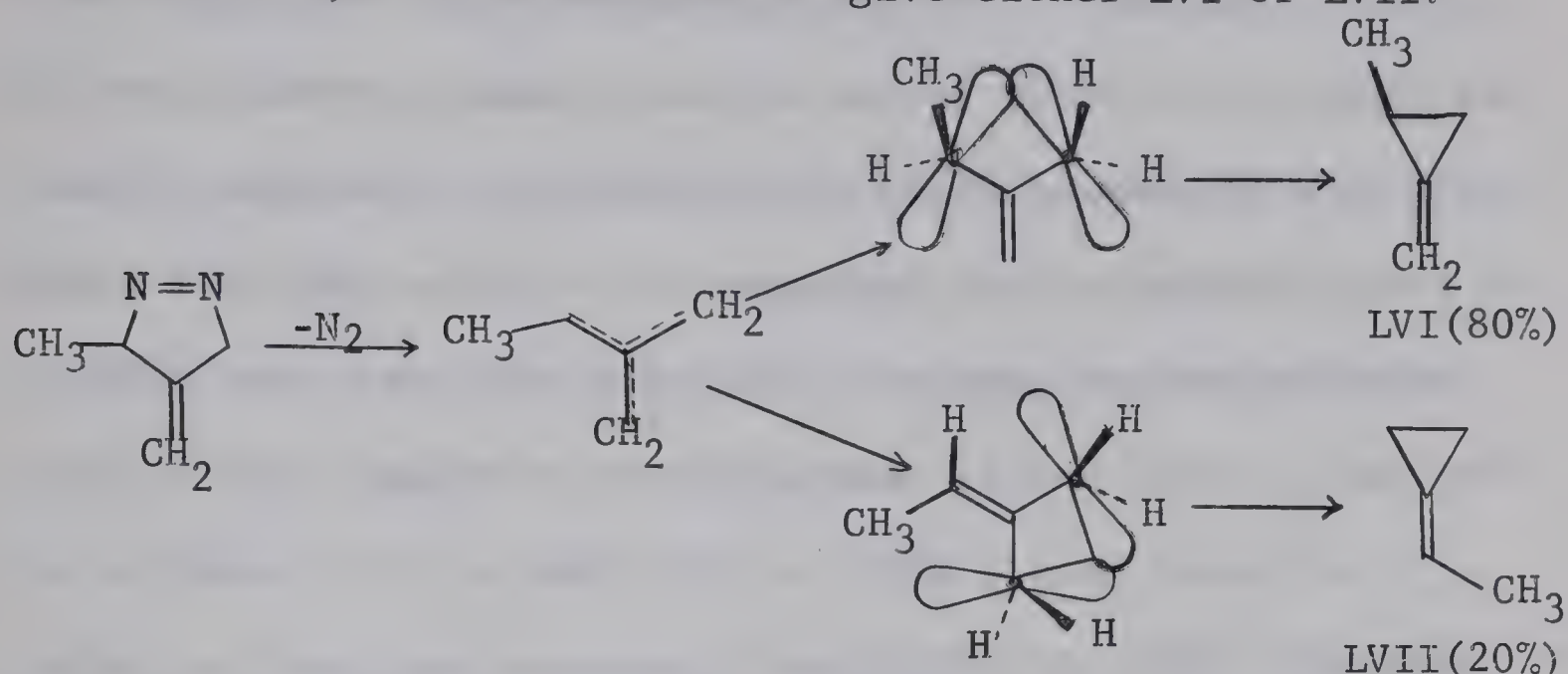
out by a control experiment. Heating a mixture of LIIa (59.3%) and LIIb (40.7%) at 250° for two hours (>10 half-lives) gave the thermodynamic equilibrium mixture which was found, by nmr (Figure 24), to be composed of $67.6 \pm 0.7\%$ LIIa and $32.4 \pm 0.7\%$ LIIb. Since thermolysis of XLVI produces 59.3% LIIa and 40.7% LIIb both products must arise directly from the intermediate and a "hot" LIIa is not involved.

A similar equilibrium mixture LIIIa (67%) and LIIIb (33%) was produced when LIIIa, prepared by the addition of diazomethane to allene- d_4 in the presence of cuprous chloride, was heated in *o*-dichlorobenzene solution at 251° in an nmr tube. The same sample had previously been used to show that the rate of interconversion of LIIIa and LIIIb is, within our experimental error, the same as the rate of interconversion of 2-methylmethylenecyclopropane (LVI) and ethylidenecyclopropane (LVII).⁵⁷

Thermolysis of XLVII in solution gave LIIIa ($72.4 \pm 1.0\%$) which is approximately the same mixture that was obtained in the gas phase thermolysis. This observation provides further evidence against a "hot" LIIIa intermediate because a "hot" species is expected to be collisionally deactivated more rapidly in solution than in the gas phase.

Chesick⁵⁷ has studied the thermal interconversion of (LVI) and (LVII) and suggests that a substituted trimethylene-intermediate (LV) may be involved. Thermolysis of 3-methyl-4-

methylene-1-pyrazoline (LIV) is expected to give a similar intermediate, which can close to give either LVI or LVII.



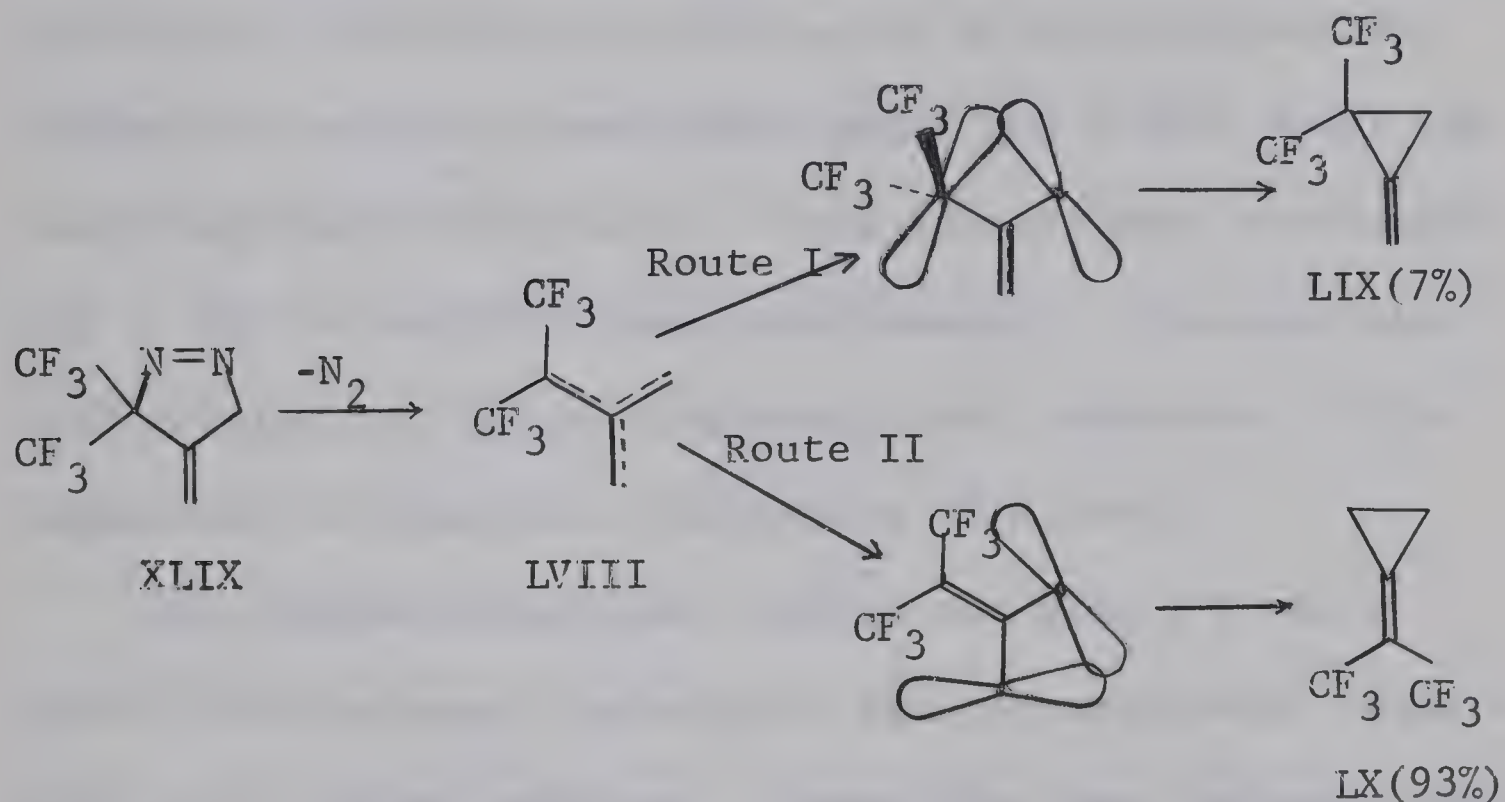
Analysis by g.c. indicates that actual product mixture is LVI(80%) and LVII(20%). Both products give nmr spectra that are identical to those reported by Chesick. The spectrum of the major product consists of a multiplet at τ 4.75, a multiplet at τ 8.75 superimposed on a doublet at τ 8.88($J=7$ c.p.s.) and a multiplet at τ 9.3 with area ratios of approximately 2:5:1. The minor product gives a multiplet at τ 4.37, a doublet of quintets at τ 8.23($J=7$ and 2 c.p.s.), and a multiplet at τ 9.03 at area ratios of 1:3:4.

Enthalpy considerations can be used to explain the higher yield of LVI. The product-determining transition state between LV and LVII has two primary "radicals" and the one between LV and LVI has a primary and a secondary "radical". The standard heats of formation of 2-methyl-1-butene and 2-methyl-2-butene are known to be -8.68 and -10.17 kcal, respectively.⁷⁴ Removal of a primary and a secondary H atom from the

former would give a species similar to that predicted for the transition state between LV and LVI. Similarly, removal of two primary H atoms from the latter would give a species that is similar to the transition state between LV and LVII. Since the bond energy of a secondary carbon-hydrogen bond is 3.5 ± 0.5 kcal less than that for a primary carbon-hydrogen bond,⁷⁵ the transition state between LV and LVI is expected to be about $3.5 - (-8.68 + 10.17) = 2.0 \pm 0.5$ kcal lower in enthalpy than that between LV and LVII. At 180° this will amount to $e^{-2.0/RT} = 1/9.2$ in the ratio of products LVII/LVI. Since there are two possible modes of formation of LVI from LV and only one mode of formation of LVII from LV, the expected ratio of LVII/LVI would then be about 1/18.4. This corresponds to yields of LVI(95%) and LVII(5%), which is reasonably close to the observed yields, LVI(80%) and LVII(20%).

Thermolysis of 3,3-bis(trifluoromethyl)-4-methylene-1-pyrazoline (XLIX) produces two products, LIX(7%) and LX(93%). Analysis and separation of the products was achieved by g.c.. The MS-9 mass spectrum of each product shows that both have the formula, $C_6H_4F_6$. The nmr spectrum of the major product in carbon tetrachloride solution consists of a septet at $\tau 8.45$ ($J = 1.8$ c.p.s.) consistent with four equivalent protons coupled to six equivalent fluorines as expected for structure LX. The minor product has multiplets at $\tau 4.22$ and

8.05 which have equal integrated intensities, in accordance with structure LIX. The higher yield of LX can also be explained from enthalpy considerations. Since the trifluoromethyl groups are electron-withdrawing the "radicals" in the transition state produced via Route I are expected to be destabilized. The lower energy path from the intermediate (LVIII) to a product would therefore be Route II.



CHAPTER IV

E X P E R I M E N T A L

All boiling points and melting points are uncorrected.

The infrared spectra were obtained on a Perkin-Elmer Model 421 spectrophotometer equipped with grating optics. Nuclear magnetic resonance spectra were measured using Varian Associates Models A-60 and HA-100 spectrometers. The ultraviolet spectra were obtained on a Perkin-Elmer 202, ultraviolet-visible spectrophotometer and a Cary Model 14M recording spectrophotometer. Mass spectra were obtained on A.E.I. MS-2-H and MS-9 mass spectrometers. Microanalyses were carried out in the Microanalytical Laboratory of the Department of Chemistry, University of Alberta.

Gas chromatography was carried out with a F and M Model 500 programmed temperature gas chromatograph, using a variety of column packings. Preparative gas chromatography was carried out on a Nestor Faust "Prepkromatic 850". The refractive indices were measured on a Bausch and Lomb refractometer.

(A) Preparations

3-Vinyl-1-pyrazoline (XXVI). To a solution of diazomethane⁷⁶ at -78° (6 g, 0.14 moles) in 300 ml of ether was added butadiene (15 g, 0.28 moles) and the solution was allowed to come to room temperature. After the mixture had been kept at 25° for one day in a pressure bottle the

yellow color of diazomethane had disappeared. After evaporation of the ether and excess butadiene, distillation of the residue through a short Vigreux column gave 11 g (80%) of a product b.p. 72-75°/40 mm, n_D^{25} 1.4665. The ultraviolet spectrum in ethanol displayed a maximum at 322 mμ (ϵ = 336, C₂H₅OH). The nmr spectrum is displayed in Figures 5 and 6. The infrared spectrum is shown in Figure 3.

Anal. Calcd. for C₅H₈N₂: C, 62.5; H, 8.34; N, 29.2

Found: C, 62.7; H, 8.53; N, 28.7

3-Isopropenyl-3-methyl-1-pyrazoline (XXVII). To 100 ml of an ether solution of diazomethane (6 g., 0.14 moles) was added 2,3-dimethylbutadiene (15 ml, 0.16 moles). The mixture was kept in a closed vessel, in the dark, for 3 days. The resulting solution was fractionated through a short column to produce 6 g of a colorless liquid, b.p. 66-67°/10 mm, n_D^{25} 1.4653. The ultraviolet spectrum in ethanol displayed a maximum at 324 mμ (ϵ = 148, C₂H₅OH). The infrared and nmr spectra are displayed in Figures 4 and 7 respectively.

Anal. Calcd. for C₇H₁₂N₂: C, 67.70; H, 9.74; N, 22.56

Found: C, 67.65; H, 9.68; N, 22.60

4-Methylene-1-pyrazoline (XXXIX). An ether solution of diazomethane (6 g in 300 ml. of ether) was dried by allowing the solution to stand over KOH or NaOH pellets for several hours. It was then distilled, behind a shield and in a fume hood, until the boiling point was

32° (700 mm). This procedure concentrated the diazomethane to about 6 g in 50-80 ml. of ether. Thirty ml. of liquid allene was then added and the mixture was kept in a pressure bottle at 27° for 15-20 hours. The ether and excess allene was evaporated under "vacuo" and the residue was vacuum distilled through a 30 cm. Vigreux column as quickly as possible. The yield was 8 g (69%), b.p. 49-50 (33 mm), n_D^{25} 1.4714. The nmr and infrared spectra are reproduced in Figures 13 and 16 respectively. The ultraviolet spectrum has a λ_{\max} at 322 m μ (ϵ = 490, 95% ethanol).

Anal. Calcd. for C₄H₆N₂: C, 58.6; H, 7.3; N, 34.1.

Found: C, 58.3; H, 7.8; N, 33.8.

Diazomethane-d₂ was prepared according to the method of Leitch et al, except that the exchange was carried out in a cold room at 0°; yield, about 3 g (50%) in 300 ml. of ether. Redistillation gave a more concentrated solution of diazomethane-d₂ (3 g in 80 ml. of ether).

4-Methylene-1-pyrazoline-3,3-d₂ (XLVI). To the concentrated ether solution of diazomethane-d₂ (about 3 g in 80 ml. of ether) in a pressure bottle was added approximately 30 ml. of liquid allene and the mixture was kept for 15-20 hours at room temperature. After evaporation of the ether and excess allene, the residue was rapidly vacuum distilled through a 30 cm. Vigreux column; yield, 2 g (35%). The boiling point, refractive index, and ultraviolet spectrum

are the same as those for XXXIX. The MS-2-H mass spectrum shows that the molecular ion has a mass of 84. The nmr spectrum (Figure 14) shows that XLVI is 92-95% deuterated.

Allene-d₄ was prepared by the method of Morse and Leitch.⁷¹ Approximately 15 ml. of liquid was obtained which was allene-d₄ (66%) and propyne-d₄ (34%). Most of the propyne-d₄ was removed by passing the mixture, in the gaseous state, through two portions of an ammoniacal silver nitrate solution. The solution was prepared by dissolving silver nitrate (60 g) in 400 ml. of water and adding ammonia solution until the original precipitate dissolved. A g.c. analysis indicated that the gas was 98% allene-d₄.

4-Methylene-1-pyrazoline-3,3,6,6-d₄ (XLVII). To a solution of diazomethane (5 g , 0.12 moles) in 60 ml. of ether was added allene-d₄ (6 g , 0.14 moles). The mixture was kept in a pressure bottle at room temperature for 20 hours. After the ether and unreacted diazomethane and allene-d₄ were evaporated, the residue was vacuum distilled; yield, 4 g (40%). The colorless liquid obtained had a refractive index, ultraviolet spectrum, and boiling point that were the same as those of XXXIX. The nmr spectrum (Figure 15) indicated that the 3 and 6-positions were >95% deuterated.

4-Methylene-1-pyrazoline-3,3,5,5,6,6-d₆ (XLVIII) was prepared by reacting allene-d₄ (6 g , 0.14 moles) with diazo-

methane- \underline{d}_2 (3 g , 0.07 moles) in 80 ml. of ether. After storage for 20 hours at room temperature, evaporation of the ether, and a rapid vacuum distillation through a 30 cm. Vigreux column, XLVIII was obtained as a colorless liquid; yield, 2 g (33%). Its boiling point, refractive index and ultraviolet spectrum were the same as those for XXXIX. The infrared spectrum showed only a small amount of absorption between 2050 and 2250 cm^{-1} . From previous preparations involving diazomethane- \underline{d}_2 and allene- \underline{d}_4 , XLVIII was estimated to be $95 \pm 3\%$ deuterated.

Ethyl N-ethyl-N-nitrosocarbamate was prepared by the method of Hartman and Phillips⁷⁸ except ethyl N-methylcarbamate was replaced by ethyl N-ethylcarbamate. The yield of pink liquid, b.p. 52.5-53.5 (5 mm.), was 122 g (84%).

3-Methyl-4-methylene-1-pyrazoline (LIV). Ethyl N-ethyl-N-nitrosocarbamate (25 g , 0.17 moles) was added dropwise to a magnetically stirred solution of potassium hydroxide (25 g , 0.45 moles) in 100 ml. of n-propyl alcohol. A slow stream of nitrogen carried the diazoethane that was produced into 100 ml. of decalin at -40° . The decalin solution was warmed to 25° ; then nitrogen was passed slowly through it and into allene (12 g , 0.30 moles) at -78° until the orange-yellow color stopped increasing in intensity. The allene-diazoethane mixture was then transferred to a small autoclave and kept at 5° for 16 hours, after which the color had

disappeared. After the allene was evaporated and the residue vacuum distilled through a short Vigreux column, 1.5 g (10%, based on ethyl N-ethyl-N-nitrosocarbamate,) of a colorless liquid was obtained, b.p. 40° (10 mm), $n_D^{25} = 1.4490$, $\lambda_{\max} = 326 \text{ m}\mu$ ($\epsilon = 290$, methanol). The nmr spectrum is reproduced in Figure 19. The molecular weight obtained from the MS-9 mass spectrum is 96.0691 (calculated for $\text{C}_5\text{H}_8\text{N}_2$, 96.0688).

bis(Trifluoromethyl) diazomethane was prepared by the method of Gale et al⁷⁰; yield 6.5 g (74%), b.p. $10 - 12^{\circ}$.

3,3-bis(Trifluoromethyl)-4-methylene-1-pyrazoline (XLIX).

bis(Trifluoromethyl) diazomethane (6.5 g, 0.036 moles) was mixed with allene in a small autoclave. The autoclave was kept at 78° for 20 hours. After the excess allene and unreacted diazo-compound were evaporated, the residue was vacuum distilled through a 6 inch Vigreux column. A colorless liquid (3 g) was obtained, b.p. 51° (30 mm.). The nmr spectrum (Figure 18) revealed that the liquid was a mixture of XLIX (25%) and its isomer L (75%). The F_{19} spectrum of the mixture has triplets at 72.09 and 72.87 ppm. from CFCl_3 ($J=0.6$ and 0.7 c.p.s. resp.).

(B) Product Analysis

The retention data for the products of thermolysis of 3-vinyl-1-pyrazoline (XXVI) are shown in Table 18. Identification of the products was accomplished by comparison of

the retention times with those of authentic samples on the columns shown. Vinylcyclopropane and cyclopentene were further confirmed when the particular peaks were trapped on the Prepchromatic 850 and the nmr spectrum taken.

A g.c. analysis of the thermolysis products of 4-methylene-1-pyrazoline showed that only nitrogen and one other product were produced. The other product had an identical retention time (9.0 min.) as an authentic sample of methylenecyclopropane on a 20 ft. squalene on chromosorb-P column at 30°. This observation as well as the nmr spectrum, which in carbon tetrachloride solution consists of a quintet ($J=2.2$ c.p.s.) at $\tau 4.65$ and a triplet ($J=2.2$ c.p.s.) at $\tau 8.95$ at an intensity ratio of 1:2, confirmed that the product was methylenecyclopropane.⁷⁹

Most of the authentic samples for g.c. comparison were readily available except for the following two compounds.

Vinylcyclopropane was prepared by the addition of methylene iodide to butadiene in the presence of a zinc-copper couple as described by Overberger and Halek;⁸⁰ yield, 0.7 g (11%); reported, 26%.

Methylenecyclopropane was prepared by reacting 3-chloro-2-chloromethylpropene with magnesium in tetrahydrofuran solution as described by Grayson et al⁸¹, yield (3 g, 40%) by g.c. The product was obtained as a mixture with tetrahydrofuran. It was used without further purification, since only its

TABLE 18

RETENTION DATA FOR THE THERMOLYSIS PRODUCTS OF XXVI

Column	Column Temp. (°C)	Helium Flow Rate (ml/min)	Compd.	Retention Time (min. from air)
20' X 1/4"	0	60	butadiene	5.8
	0	60	1,4-pentadiene	9.4
β,β -oxydipropionitrite	0	60	cyclopentene	15.4
	0	60	<u>trans</u> -1,3-penta- diene	21.6
10% on chromosorb W	0	60	<u>cis</u> -1,3-pentadiene	26.0
	0	60	vinylcyclopropane	28.7
	0	60	cyclopentadiene	42.5
	40	60	butadiene	1.58
	40	60	1,4-pentadiene	2.17
	40	60	cyclopentene	3.48
	40	60	<u>trans</u> -1,3-penta- diene	4.5
	40	60	<u>cis</u> -1,3-pentadiene	5.2
	40	60	vinylcyclopropane	5.5
20' X 1/4"	65	70	butadiene	3.0
	65	70	1,4-pentadiene	6.3
squalene 25%	65	70	cyclopentadiene	8.9
	65	70	<u>trans</u> -1,3-penta- diene	10.4
on chromosorb P	65	70	vinylcyclopropane	10.5
	65	70	<u>cis</u> -1,3-pentadiene	11.4
	65	70	cyclopentene	14.4
8' X 1/4"	0	60	butadiene	2.4
	0	60	1,4-pentadiene	4.6
dimethylsulfolane	0	60	cyclopentene	8.4
	0	60	<u>trans</u> -1,3-penta- diene	11.7
10% on chromosorb W	0	60	<u>cis</u> -1,3-pentadiene	13.2
	0	60	vinylcyclopropane	13.3
	0	60	cyclopentadiene	17.2

retention time was required.

The following procedure was used to obtain the yields of the deuterated methylenecyclopropanes produced by thermolysis

of the deuterated 4-methylene-1-pyrazolines, XLVI and LXVII. When the thermolysis was complete, the reactor was opened to the rack, which contained nitrogen at approximately the same pressure as that inside the reactor. During the evacuation, the gases were passed through a trap at -196° . After complete evacuation, the system was closed and the products were distilled from the trap into a nmr tube that contained carbon tetrachloride and tetramethylsilane. The proportions of each deuterated isomer were calculated from the ratio of ring protons (τ 8.95) to vinyl protons (τ 4.65) in the nmr spectrum.

(C) Control Experiments

(i) 3-Vinyl-1-pyrazoline-5,5- \underline{d}_2 (XXXII) (0.4 g , 0.004 moles) was thermolyzed at 140° in a 500 ml. round bottom flask fitted with an adapter containing a stopcock and a ball joint. When the thermolysis was complete, the hydrocarbons were transferred by a trap to trap distillation to a gas injection cell, from which they were injected into the helium stream of the Prep-kromatic 850. After the products were separated using a $3/8'' \times 20'$ dimethylsulfolane on chromosorb W column, the cyclopentene- \underline{d}_2 peak was trapped. When the procedure was repeated a total of approximately 8 mg was accumulated. The product was then transferred on the vacuum rack to an nmr tube containing carbon tetrachloride and tetramethylsilane. The absence of any resonance at τ 8.2 in the HA-100 spectrum indicated that all of the deuterium was at C_4 .

(ii) Several thermolyses of XXXII were carried out in the reactor at $180 \pm 5^\circ$. At this temperature the half-life was estimated to be about 10 seconds. The products were trapped in the usual manner and transferred by a trap to trap distillation into a gas injection cell. They were then injected into the Prepchromatic 850 and separated using a $1/4'' \times 20'$ β, β -oxydipropionitrile on Chromosorb W column. The cyclopentene- d_2 and vinylcyclopropane- d_2 were trapped and transferred to separate nmr tubes containing carbon tetrachloride and tetramethylsilane. The cyclopentene- d_2 spectrum consisted of a singlet at $\tau 4.38$ and multiplets at $\tau 7.71$ and 8.20 at intensity ratios of $1:00:1.48:0.53$, which corresponds to a mixture of cyclopentene-3,3- d_2 ($53 \pm 3\%$) and cyclopentene-4,4- d_2 ($47 \pm 3\%$). The multiplets at $\tau 5.12$ and 4.69 in the vinylcyclopropane- d_2 spectrum had an intensity ratio of $2.07 \pm 0.10:1.00$, indicating that the number of terminal methylene protons was twice that of methinyl protons, and that of all of the deuterium was in the ring.

The non-condensable gases were also analyzed by mass spectrometry after one of the runs. The ratio of $HD:H_2:D_2$ was found to be $40.8:58.5:0.8$.

(iii) In order to make sure that it is stable under the high temperature thermolysis conditions, $100 \mu l$ of vinylcyclopropane was injected into the reactor. After one hour at 180° , the recovered liquid was shown to be pure vinylcyclopropane by

g.c. analysis. Similarly, cyclopentene was recovered unchanged after one hour in the reactor at 180°.

(iv) An experiment was designed to determine whether or not any scrambling of deuterium takes place in 4-methyl-1-pyrazoline-3,3,6,6,- \underline{d}_4 (XLVII) under the reaction conditions. A sample was injected into the reactor at 166° as in a normal run. After 12 minutes (one half-life) the reactor was then evacuated and its contents were collected in a trap at -196°. The trap was then warmed to 0° and the methylenecyclopropane- \underline{d}_4 was pumped off. The remaining liquid was transferred by a trap to trap distillation to an nmr tube containing carbon tetrachloride and tetramethylsilane. The nmr spectrum was identical to that of the initial XLVII, which indicates that no deuterium scrambling occurs under the reaction conditions.

(v) An experiment was conducted to determine the thermodynamic equilibrium mixture of LIIa and LIIb. A 30 μ l sample of the product mixture (LIIa, 59.3% and LIIb, 40.7%) from thermolysis of XLVI was placed into a 20 ml. break seal. The break seal was heated in refluxing cinnamaldehyde (250°) for two hours (>10 half-lives). It was then joined to a vacuum rack and its contents were transferred by a trap to trap distillation to a nmr tube that contained carbon tetrachloride and tetramethylsilane. The nmr spectrum (Figure 24) showed that $R/V = 1.96 \pm 0.04$, which corresponds to LIIa (67.6%) + LIIb (32.4%).

(vi) Preparation and Isomerization of Methylene-
cyclopropane-2,2,4,4-d₄ (LIIIIa). Allene-d₄ (5 g 0.11 moles)
at -78° was placed into a cold 200 ml. three-necked flask
containing cuprous chloride (0.5 g , 0.005 moles). The
flask was fitted with a dry ice condenser and a dropping
funnel. After the allene-d₄ had warmed enough to reflux,
diazomethane (3 g , 0.07 moles) in 40 ml. of ether was
added dropwise with magnetic stirring. The addition was
carried out in a fume hood and behind a shield. Stirring was
continued for an additional 30 minutes after the addition was
complete. A g.c. analysis indicated the presence of methylene-
cyclopropane-d₄; yield, approximately 0.5 g (13%). About
10 mg. of the product was separated from the ether and allene-d₄
by preparative g.c. using a 3/8" X 20' Ucon on Chromosorb W
column. It was then transferred to a thick walled nmr tube
containing o-dichlorobenzene. The nmr spectrum showed that
 $R/V = 8.8 \pm 0.4$ which corresponds to LIIIIa (90%) + LIIIIb (10%).

The ratio R/V did not change after the nmr tube was kept
at 181° for one hour. After 16 hours at 180° the ratio
dropped to 7.1 ± 0.4 . The half-life for equilibration of LVI
and LVII is 2.0 hours at 212°. ⁵⁷ When the nmr tube was kept
at 212° for 2.0 hours R/V became 3.7 ± 0.3 , which is within
experimental error of the ratio 3.4 that is estimated for one
half-life. After one hour at 251° the thermodynamic equilib-
rium mixture was obtained, for which R/V was 2.04 ± 0.10 .

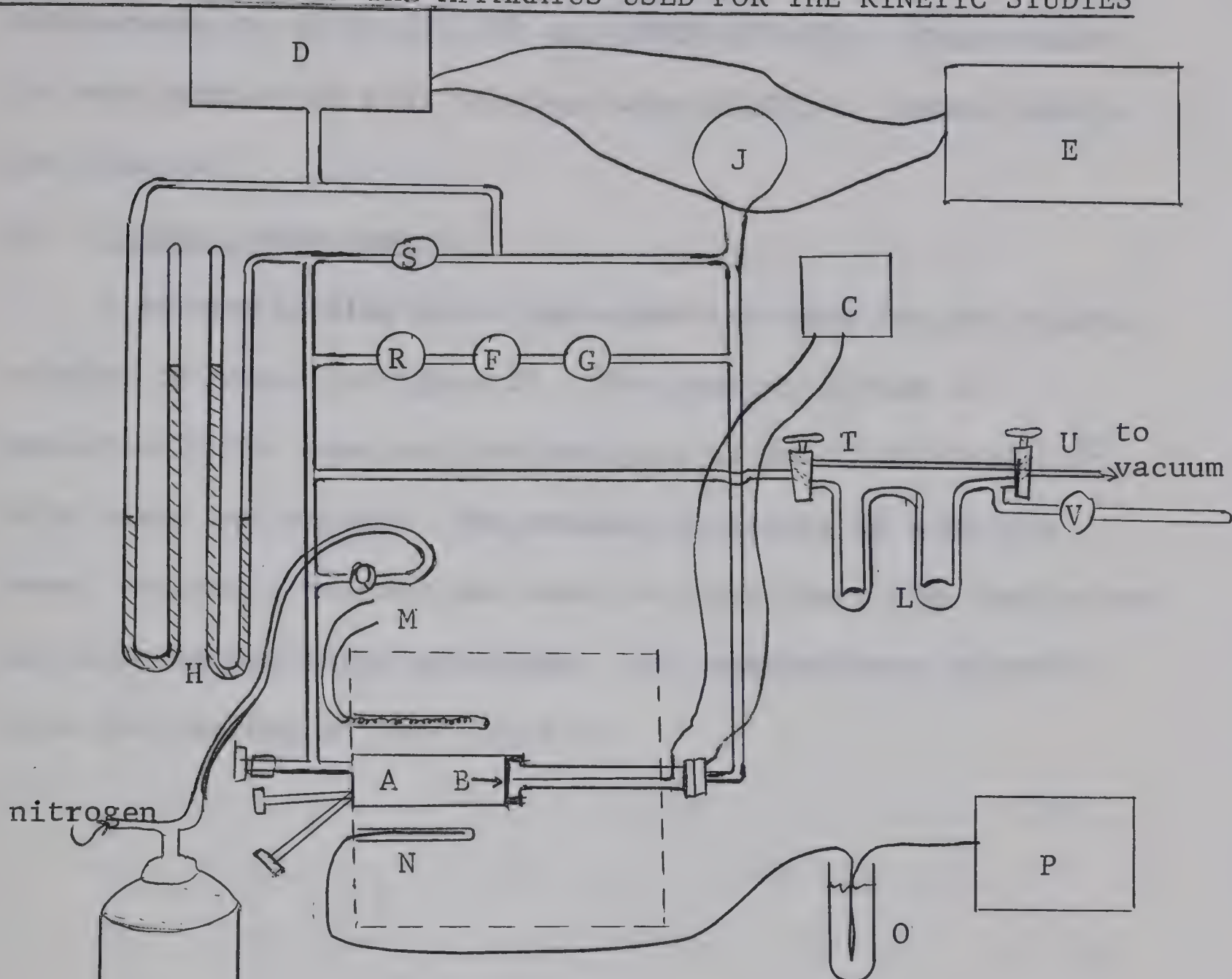
(vii) Attempts to Add Trimethylenemethane to Cyclohexene and Diethylfumarate. Cyclohexene (3 g , 0.037 moles) and XXXIX (0.5 g , 0.006 moles) were added to a 10 ml. autoclave. The autoclave was then heated at 190° for 30 minutes in an oil bath to thermolyze the XXXIX. A programmed temperature g.c. analysis of the resulting mixture indicated that only methylene-cyclopropane and cyclohexene were present. The C₁₀ region, as judged by the retention times of cis- and trans-decalin, was completely free of any peaks. Under the conditions of the analysis a 0.1% yield of the adduct would have easily been observed.

In an identical experiment, except that cyclohexene was replaced by diethylfumarate, no trimethylenemethane adduct was observed.

(viii) Decomposition of 4-Methylene-1-pyrazoline-3,3,6,6-d₄ (XLVII) in Decalin Solution. A 50 ml. three-necked flask with 14/20 joints was fitted with a reflux condenser and a special stopper that contained a rubber septum. A gas burette was connected to the top of the reflux condenser. Decalin (20 ml.) was added to the flask and heated to reflux (185°). A 100 μl sample of XLVII was then injected into the liquid. When gas evolution ceased, a slow stream of nitrogen was passed through the entire system, forcing all of the gases to pass through a trap at -196°. The methylenecyclopropane-d₂ in the trap was distilled into an nmr tube containing carbon tetrachloride and

FIGURE 25

SCHEMATIC DIAGRAM OF THE APPARATUS USED FOR THE KINETIC STUDIES



A = Reactor

B = Diaphragm

C = Relay

D = Transducer

E = Recorder

F = Calibrated needle
valve

G = Solenoid valve

H = Manometers

J = Small ballast

K = Large ballast

L = Cold traps

M = Heaters

N = Thermocouples

O = Cold junction

P = Potentiometer

Q,R,S,T,U,V = Stopcocks

tetramethylsilane. In the nmr spectrum $R/V = 2.62 \pm 0.10$, which corresponds to LIIIa (72.4%) and LIIIb (27.6%). This result is very similar to that obtained when XLVII is thermolyzed in the reactor.

(D) Kinetic Measurements

A schematic diagram of the apparatus used for the kinetic studies is shown in Figure 25. The reactor system is essentially the same as that designed by Smith and Bagley,⁸² with minor variations. The working procedure is also the same. Mishra's reactor was used but there were some variations in the attached glass apparatus. All samples were injected into the reactor as neat liquids.

B I B L I O G R A P H Y

1. A. Mishra, Ph.D. Thesis, University of Alberta 1965.
2. R.J. Crawford, R.J. Dummel, and A. Mishra, J. Am. Chem. Soc., 87, 3023(1965).
3. R.J. Crawford and A. Mishra, ibid, 87, 3768(1965).
4. R.J. Crawford, A. Mishra, and R.J. Dummel, ibid, 88, 3959(1966).
5. R.J. Crawford and A. Mishra, ibid, 88, 3963(1966).
6. R.B. Woodward and R. Hoffmann, ibid, 87, 395(1965)
7. R. Hoffmann, Abstracts of the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Paper 109K.
8. G. Erickson, M.Sc. Thesis, University of Alberta (1966).
9. D.E. McGreer and N.S. Wu, Can. J. Chem., In Press.
10. D.W. Setzer and B.S. Rabinovitch, J. Am. Chem. Soc., 86, 564(1964).
11. S. Seltzer, ibid, 83, 2625(1961).
12. S. Seltzer, ibid, 85, 14(1963).
13. S. Seltzer and F.T. Dunne, ibid, 87, 2628(1965).
14. S. Seltzer and E.J. Hamilton Jr., ibid, 88, 3775(1966).
15. M. Wolfsberg and M. Stern, Pure Appl. Chem., 8, 225(1964).
16. M. Wolfsberg and M. Stern, ibid, 8, 325(1964).
17. J.H. Schachtschneider and R.J. Snyder, Spectrochim. Acta., 19, 117(1963).
18. J. Bigeleisen, J. Chem. Phys. 17, 675(1949).

19. J. Bigeleisen, J. Phys. Chem., 56, 823(1952).
20. S. Seltzer, J. Am. Chem. Soc., 83, 1861(1961).
21. A. Streitwieser Jr., R.H. Jagow, R.C. Fahey, and S. Suzuki, ibid, 80, 2326(1958).
22. S.W. Benson, J. Chem. Phys., 34, 521(1961).
23. F.T. Smith, ibid, 29, 235(1958).
24. a) B.S. Rabinovitch, E.W. Schlag, and K.B. Wiberg, ibid, 28, 504(1958).
b) M.C. Flowers and H.M. Frey, Proc. Roy. Soc., 257, 122(1960).
25. M.C. Flowers and H.M. Frey, J. Chem. Soc., 3547, (1961).
26. C.A. Wellington, J. Phys. Chem., 66, 1671(1962).
27. H.M. Frey and D.C. Marshall, J. Chem. Soc., 3981(1962).
28. R.J. Ellis and H.M. Frey, ibid, 959(1964).
29. R.J. Ellis and H.M. Frey, ibid, 5578(1964).
30. Chambers and Kistiakowsky, J. Am. Chem. Soc., 56, 399(1934).
31. H.M. Frey, Trans. Faraday Soc., 58, 516(1962).
32. W.A. Gibbons, W.F. Allen, and H.E. Gunning, Can. J. Chem., 40, 568(1962).
33. W.A. Gibbons, M. Sc. Thesis, University of Alberta (1961).
34. S.W. Benson, J. Chem. Phys., 34, 521(1961).
35. B.S. Rabinovitch, E. Tschuikow-Roux and E.W. Schlag, J. Am. Chem Soc., 81, 1081(1959).
36. M.C. Flowers and H.M. Frey, J. Chem. Soc., 3953(1959).

37. E. Muller and E. Roser, J. Prakt. Chem., 133, 291(1932).
38. D.E. McGreer, N.W.K. Chiu, M.G. Vinje, Can. J. Chem., 43, 1398(1965).
39. J.J. Uebel and J.C. Martin, J. Am. Chem. Soc., 86, 4618 (1964).
40. R.R. Fraser, Can. J. Chem., 40, 78(1962).
41. A.N. Frost and R.L. Pearson, "Kinetics and Mechanism", John Wiley and Sons Inc., New York, 2nd Edition, p.9-100(1961).
42. F. Daniels, et al, "Experimental Physical Chemistry," McGraw-Hill Book Company Inc., Fifth Edition. p.339(1956).
43. L.P. Hammet, "Introduction to Physical Chemistry," McGraw-Hill Book Company Inc., 1952, p.410.
44. J.L. Franklin and F.H. Field, J. Am. Chem. Soc., 75, 2819(1953).
45. M. Swarc and A.H. Sehon, J. Chem. Phys., 18, 237(1950).
46. A.S. Gordon, S.R. Smith, and J.R. McNesby, J. Am. Chem. Soc., 81, 5059(1959).
47. S.W. Benson, A.N. Bose, and P. Nangia, ibid, 85, 1388(1963).
48. M.R. Willcott and V.R. Cargle, J. Am. Chem. Soc., 89, 724(1967).
49. C.S. Elliot and H.M. Frey, J. Chem. Soc., 4289(1965).
50. D.W. Vanus and W.D. Walters, J. Am. Chem. Soc., 70, 4035(1948).
51. G.J. Janz, "Estimation of Thermodynamic Properties of Organic Compounds," Academic Press Inc., New York (1958).

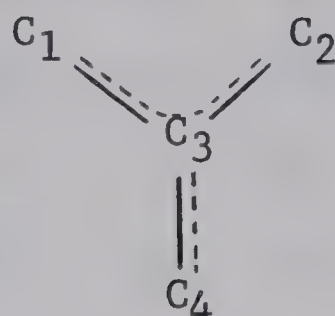
52. "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Am. Petroleum Institute, Res. Proj., Carnegie Press (1953)
53. H. Dauben, private communication.
54. R.C. Reid and T.K. Sherwood, "The Properties of Gases and Liquids. Their Estimation and Correlation," McGraw-Hill Book Co., Second Edition, 1966, Chapter 5.
55. B.S. Rabinovitch and M.C. Flowers, Quarterly Reviews, 18, 122(1964).
56. J.D. Roberts, "Notes on Molecular Orbital Calculations," W.A. Benjamin, Inc., New York, 1962, p.53.
57. J.P. Chesick, J. Am. Chem. Soc., 85, 2720(1963).
58. E.F. Ulmann, ibid, 82, 505(1960).
59. H.M. Frey, Trans. Faraday Soc., 57, 951(1961).
60. W. v.E. Doering, private communication and footnote in ref. 57.
61. G.F. Emerson, L. Watts and R. Pettit, J. Am. Chem. Soc., 87, 131(1965).
62. G.F. Emerson, K. Ehrlich, W.P. Giering and P.C. Lauterbar, ibid, 88, 3172(1966).
63. P. Dowd, ibid, 88, 2587(1966).
64. P. Dowd, and K. Sachdev, ibid, 89, 715(1967).
65. S.D. Andrews and A.C. Day, Chem. Comm., 667(1966).
66. W.L. Mock, Ph.D. Thesis, Harvard University (1964).
67. W.T. Borden, Tetrahedron Letters, 259(1967).

68. P. Dowd, private communication.
69. R.J. Crawford and D.M. Cameron, J. Am. Chem. Soc., 88, 2589(1966).
70. I.A. D'yakonov, J. Gen. Chem., (U.S.S.R.) 15, 473(1945), C.A. 40:4718.
71. A.T. Morse and L.C. Leitch, J. Org. Chem., 23, 990(1958).
72. D.M. Gale, W.J. Middleton and C.J. Krespen, J. Am. Chem. Soc., 88, 3617(1966).
73. a) A.E. Stearn and H. Eyring, J. Chem. Phys., 3, 778(1935).
b) S. Glasstone, K.J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York (1941), p.333.
74. F.D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Carnegie Press, (1953), p.475.
75. a) S.W. Benson, J. Chem. Ed., 42, 502(1965).
b) G.C. Fettis, J.H. Knor, and A.F. Trotman-Dickenson, J. Chem. Soc., 4177(1960).
76. J.A. Moore and D.E. Reed, Organic Synthesis, 41, 16(1961).
77. L.C. Leitch, P.E. Gagnon, and A. Cambron, Can. J. Research, 28B, 256(1950).
78. W.W. Hartman and R. Phillips, ibid, Coll. Vol. II, 464(1943).
79. B.C. Anderson, J. Org. Chem., 27, 2720(1962).
80. C.G. Overgerger and G.W. Halek, J. Org. Chem., 28, 867 (1963).

81. J.T. Grayson, K.W. Greenlee, J.M. Defer, and C. Boord,
J. Am. Chem. Soc., 75, 3344(1953).
82. G.G. Smith and F.D. Bagley, Rev. Sci. Instr., 32, 703
(1961).
83. I. Heilbron and H.M. Bunbury, "Dictionary of Organic
Compounds", Vol. III, Eyre and Spottismende, London,
p. 497 (1953).

APPENDIX I

HUCKEL MOLECULAR ORBITAL CALCULATIONS ON TRIMETHYLENEMETHANE



The values of the energy levels (E) are obtained from the roots of the following secular determinant.¹

$$\begin{vmatrix} H_{11} - S_{11}E & H_{12} - S_{12}E & H_{13} - S_{13}E & H_{14} - S_{14}E \\ H_{12} - S_{12}E & H_{22} - S_{22}E & H_{23} - S_{23}E & H_{24} - S_{24}E \\ H_{13} - S_{13}E & H_{23} - S_{23}E & H_{33} - S_{33}E & H_{34} - S_{34}E \\ H_{14} - S_{14}E & H_{24} - S_{24}E & H_{34} - S_{34}E & H_{44} - S_{44}E \end{vmatrix} = 0$$

The overlap integrals (S_{ij}) are assumed to be unity when $i=j$ and 0 when $i \neq j$.

$$H_{ii} = \alpha = \text{coulomb integral}$$

$$H_{ij} = \beta = \text{resonance integral (when } i \text{ and } j \text{ are adjacent atoms)}$$

$$H_{ij} = 0, \text{ when } i \text{ and } j \text{ are not adjacent}$$

The determinant now becomes

$$\begin{vmatrix} \alpha - E & 0 & \beta & 0 \\ 0 & \alpha - E & \beta & 0 \\ \beta & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

1 - J.D. Roberts, "Notes on Molecular Orbital Calculation," W.A. Benjamin, Inc., New York, (1962).

After dividing through by β and letting $(\alpha-E)/\beta=x$, the determinant becomes

$$\begin{vmatrix} x & 0 & 1 & 0 \\ 0 & x & 1 & 0 \\ 1 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

$$x \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} + \begin{vmatrix} 0 & x & 0 \\ 1 & 1 & 1 \\ 0 & 0 & x \end{vmatrix} = 0$$

$$x^2 \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - x \begin{vmatrix} 1 & 1 \\ 0 & x \end{vmatrix} - x \begin{vmatrix} 1 & 1 \\ 0 & x \end{vmatrix} = 0$$

$$x^4 - 3x^2 = 0$$

$$x(x^2 - 3)x = 0$$

$$\frac{\alpha-E}{\beta} = x = 0, \pm \sqrt{3}, 0$$

$$E = \alpha, \alpha \pm \sqrt{3}\beta, \alpha$$

The following energy level diagram can now be constructed.

$$\begin{array}{lcl} \text{---} & E = \alpha - \sqrt{3}\beta & \\ \uparrow & \uparrow & E = \alpha \\ \uparrow\downarrow & & E = \alpha + \sqrt{3}\beta \end{array} \quad E_{\pi} = 4\alpha + 2\sqrt{3}\beta$$

The four electrons would go into the levels as shown. Hund's rule states that one electron would go into each of the degenerate orbitals and that they would have identical spins,

making the molecule a triplet.

The resonance energy (DE_{π}) is given by

$$\begin{aligned} DE_{\pi} &= E_{\pi}(\text{delocalized}) - E_{\pi}(\text{localized}) \\ &= 4\alpha + 2\sqrt{3}\beta - (4\alpha + 2\beta) \\ &= 1.46\beta \end{aligned}$$

The wave functions of trimethylenemethane are of the form

$$\psi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4$$

The normalized coefficients are obtained by

$$\frac{c_n}{c_1} = + \frac{(\text{cofactor})_n}{(\text{cofactor})_1} \quad \text{if } n \text{ is odd}$$

$$\frac{c_n}{c_1} = - \frac{(\text{cofactor})_n}{(\text{cofactor})_1} \quad \text{if } n \text{ is even}$$

$$\frac{c_1}{c_1} = + \frac{\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix}}{\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix}} = \frac{x^3 - 2x}{x^3 - 2x} = 1$$

$$\frac{c_2}{c_1} = - \frac{\begin{vmatrix} 0 & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix}}{\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix}} = \frac{x}{x^3 - 2x}$$

$$\frac{c_3}{c_1} = + \frac{\begin{vmatrix} 0 & x & 0 \\ 1 & 1 & 1 \\ 0 & 0 & x \end{vmatrix}}{\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix}} = \frac{-x^2}{x^3 - 2x}$$

$$\frac{c_4}{c_1} = - \frac{\begin{vmatrix} 0 & x & 1 \\ 1 & 1 & x \\ 0 & 0 & 1 \end{vmatrix}}{\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix}} = \frac{x}{x^3 - 2x}$$

When $x = -\sqrt{3}$

n	c_n/c_1	$(c_n/c_1)^2$	c_n
1	1	1	$1/\sqrt{6}$
2	1	1	$1/\sqrt{6}$
3	3	3	$1/\sqrt{2}$
4	1	1	$1/\sqrt{6}$

$$(c_n/c_1)^2 = \sqrt{6}$$

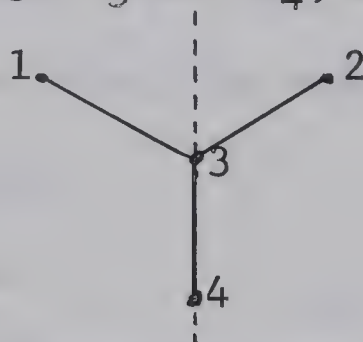
Therefore, $\Psi_1 = 1/\sqrt{6}\chi_1 + 1/\sqrt{6}\chi_2 + 1/\sqrt{2}\chi_3 + 1/\sqrt{6}\chi_4$

Similarly, the wave functions, Ψ_2 and Ψ_4 , can be calculated for $x = 0$ and $x = \sqrt{3}$.

$$\Psi_2 = 2/\sqrt{6}\chi_1 - 1/\sqrt{6}\chi_2 - 1/\sqrt{6}\chi_4$$

$$\Psi_4 = 1/\sqrt{6}\chi_1 + 1/\sqrt{6}\chi_2 - 1/\sqrt{2}\chi_3 + 1/\sqrt{6}\chi_4$$

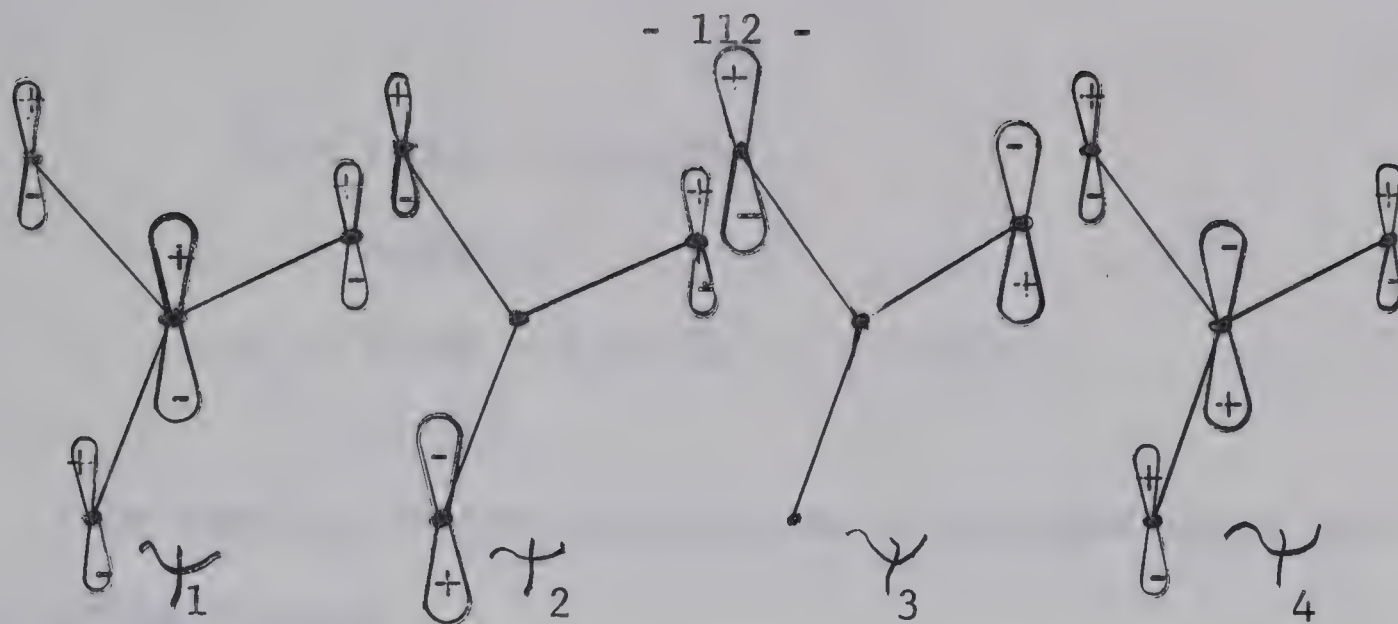
When group theory is applied to the calculation, using a C_2 symmetry axis through C_3 and C_4 , a three-row and a one-



row determinant result. The three-row determinant gives the same wave functions that were determined by the previous method, while the one-row determinant gives the fourth wave function (Ψ_3) which also has energy $E=\alpha$.

$$\Psi_3 = 1/\sqrt{2}\chi_1 - 1/\sqrt{2}\chi_2$$

The wave functions can also be represented in the following manner.



The mobile bond order (P_{ij}) can now be calculated;

$$P_{ij} = \sum_{\psi_{occ}} N c_i c_j$$

where N is the number of electrons in a given orbital.

$$P_{13} = P_{23} = P_{34} = 2 \times 1/\sqrt{6} \times 1/\sqrt{2} + 0 = 0.577$$

Since the σ -bond order is 1.0 then the total bond order is 1.577. The central carbon atom of trimethylenemethane possesses the maximum possible degree of bonding for a carbon atom ($\sum P_{ij} = 3 \times 1.577 = 4.732$) so it is used as a basis for calculations of the free valence index (F).

$$F = 4.732 - \sum P_{ij}$$

For the methylene groups

$$\begin{aligned} F &= 4.732 - (3 \times 1.0 + 1 \times 0.577) \\ &= 1.155 \end{aligned}$$

The charge distribution (q_i) is given by

$$q_i = 1.000 - \sum_{\psi_{occ.}} N c_i^2$$

$$\begin{aligned} q_1 &= 1.000 - 2(1/\sqrt{6})^2 - (2/\sqrt{6})^2 - (1/\sqrt{2})^2 \\ &= -0.500 \end{aligned}$$

$$\begin{aligned} q_2 &= 1.000 - 2(1/\sqrt{6})^2 - (-1/\sqrt{6})^2 - (-1/\sqrt{2})^2 \\ &= 0.000 \end{aligned}$$

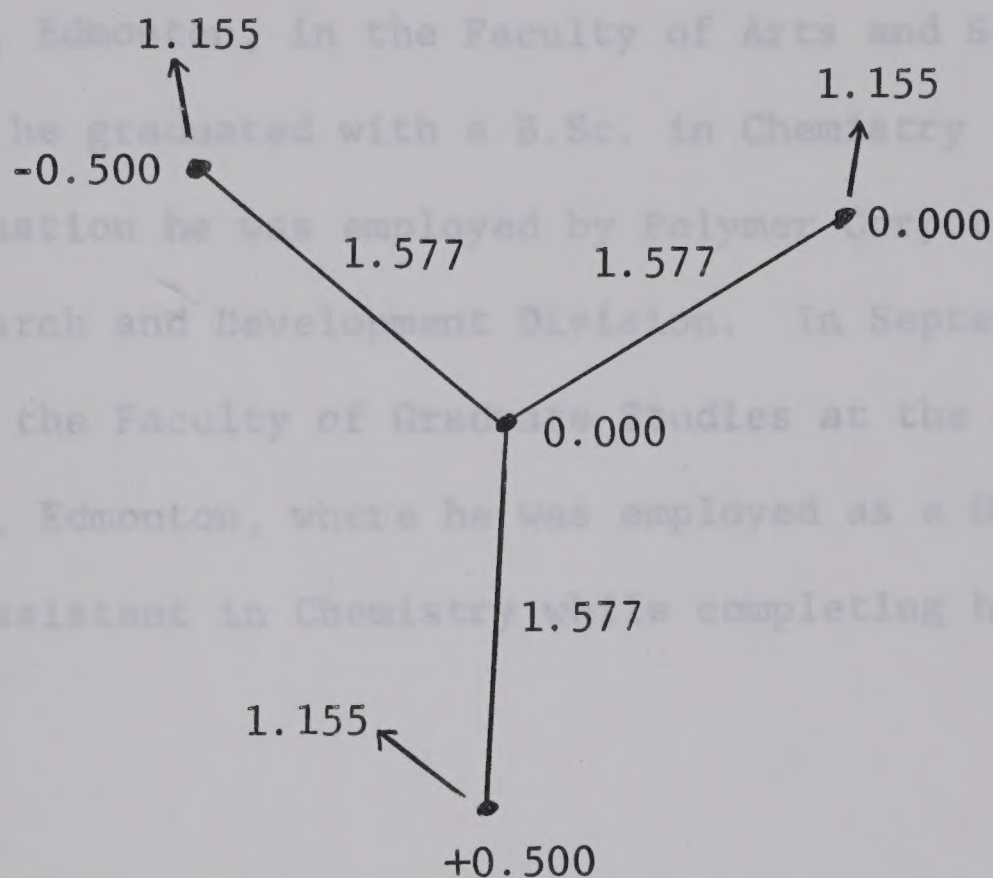
$$q_3 = 1.000 - 2(1/\sqrt{2})^2$$

$$= 0.000$$

$$q_4 = 1.000 - 2(1/\sqrt{6})^2 - (-1/\sqrt{6})^2$$

$$= +0.500$$

The results of the calculations are summed up in the following diagram.



$$DE_{\pi} = 1.46\beta$$

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